Study of the Characterization of Coals using Photoacoustic Infrared Fourier Transform Spectroscopy and Chemical Transformation and Derivatization

FINAL REPORT

by

Brian M. Lynch

(Scientific Authority: J. A. MacPhee)

DSS Contract Report No. OST85-00235

61 pp

May 21, 1987

MICROMEDIA

Study of the Characterization of Coals using Photoacoustic Infrared Fourier Transform Spectroscopy and Chemical Transformation and Derivatization

Correlation of the "Statement of Work"

in Contract File No. 20ST.23440-5-9179

with Completed Published and Unpublished Tasks

by

Brian M. Lynch

(Scientific Authority: J. A. MacPhee)

DSS Contract Report No. OST85-00235

June 22, 1987

Correlation of the "Statement of Work" in Contract File No. 20ST.23440-5-9179 with Completed Published and Unpublished Tasks

1. Correlations of PAIFT Spectral Features with Coal Properties

Our achievements in this aspect dealt with the spectroscopic properties of a series of coals subjected to high-pressure oxidations. The principal-factor-analysis approach proposed by Fredericks and co-workers did not discriminate satisfactorily among progressively oxidized coals, possibly because the series which we examined were not sufficiently different.

However, we were able to define simple relationships between a key feature of the PAIFT spectra of the coals (the levels of carbonyl content developed by vacuum drying at 100°C) and many of their characteristics (such as elemental composition, relative fluidities, percentage dilatations, melting ranges). This work is discussed in part in the manuscripts of the publications submitted as Parts 1-4 of the Final Report, and more fully in a further, expanded presentation entitled **"Detection of Surface Carbonyl Functionality of Oxidized,Vacuum-Dried Coals by PhotoAcoustic Infrared Fourier Transform (PAIFT) Spectroscopy"**, which has been submitted for publication in the American Chemical Society's Journal **Energy and Fuels**, and is supplied with this synopsis. An accompanying supplement illustrates in graphic format the details of the information summarized in Table 2 of that manuscript.

PAIFT spectra obtained on samples provided by the Scientific Authority on behalf of Professor E. Chornet were interpreted and discussed, and are reproduced in the publication "Enhancement of plastic properties of inert-rich oxidized Cretaceous coals via the water-gas shift reaction", *Fuel* **1987**, *66*, 473-478.

2. Effects on Thermal Properties of Coals of Destruction of Surface Peroxides

Thirty-three small samples of base-treated coals from the sets subjected to high-pressure oxidations were provided to the Scientific Authority for examination by thermogravimetric analysis.

3. Syntheses of Isotopically Enriched Derivatized Coals

Samples of 13C-enriched methylated coals were produced and supplied to the Scientific Authority. The solid-phase nmr spectra were acquired by Dr. J. A. Ripmeester of the National Research Council, Ottawa.

4. Curve-Resolving of PAIFT Spectra of Derivatized and Transformed Coals

This process was used in analyzing the difference spectra of the suite of high-pressure oxidized coals. The first examples of defined and separated carbonyl functionality in oxidized coals, and curve resolutions into distinct-frequency components of characteristic bandwidths, were accomplished.

5. Reduction of Ketonic Carbonyl Species in Coals

We established that it was possible to remove the ketone functions in several Canadian bituminous coals which had been oxidized by simple aerial exposure, regenerating material spectroscopically identical with the fresh coals. Removal was effected by tetrabutylammonium borohydride in aqueous tetrahydrofuran.

6. Study of "Transformations" of Lignins into Coal-like Substances

We repeated the work of Winans, which claimed that coal-like substances were generated by treatment of lignins with large quantities of clay minerals. Our results indicate that the changes occurring are just simple demethylations and dehydrations of the lignins, where the lignin hydroxy groups are etherified with those of the clay, immobilizing the polymer backbone. Such changes amount to little more than those effected by treatment of lignins with hydriodic acid .

Revision and Extension, dated October 16 1986

8. Trifluoroacetylation as a Derivatization Technique

Although anion-chromatographic analyses were successful, X-ray photoelectron spectra of the derivatized samples (obtained at CANMET by Dr. J. Brown) showed that insertion of covalent C-F and CF_2 fragments into the coals accompanies the thermal O-trifluoracetylation reactions. These results will be discussed in detail at the International Conference on Coal Science, Maastricht, The Netherlands (see Part 4 of Report).

9. Feasibility Evaluation of Reflectance FTIR Microspectrometry

Comparison of the performance of various accessories showed that the IRPLAN marketed by Spectra-Tech gives markedly superior performance to any others currently available. The spectra obtained have been supplied to the Scientific Authority.

10. Additional Statistical Analyses

Completed as a component of #1 above, and incorporated into the materials submitted for publication.

This report consists of the assembled texts of the following publications:

1. PHOTOACOUSTIC FTIR SPECTROSCOPY IN DETECTION OF COAL OXIDATION, by Brian M. Lynch and J. Anthony MacPhee.

Chapter 4 of the Book "Chemistry of Coal Weathering", Edited by Charles R. Nelson. Elsevier Publishers, Amsterdam.

2. DETECTION OF SPECIFIC TYPES OF CARBONYL GROUPS FROM CHEMICALLY AND THERMALLY PROMOTED DECOMPOSITION OF PEROXIDES ON COAL SURFACES, USING PHOTOACOUSTIC INFRARED FOURIER TRANSFORM SPECTROSCOPY, by Brian M. Lynch, Lai-Im Lancaster, and J. Anthony MacPhee.

Fuel, Volume 66, to be published in the July 1987 issue.

3. CHARACTERIZATION OF SURFACE FUNCTIONALITY OF COALS BY PHOTOACOUSTIC FTIR (PAIFT) SPECTROSCOPY, REFLECTANCE INFRARED MICROSPECTROMETRY, AND X-RAY PHOTOELECTRON SPECTROSCOPY,

by Brian M. Lynch, Lai-Im Lancaster, and J. Anthony MacPhee.

Symposium: Surface Chemistry of Coals.- Preprints, Division of Fuel Chemistry, American Chemical Society, Volume 32, No. 1, 138-145 (1987).

To be published in full in Energy and Fuels, Volume 2, issue 1 (1988).

4. CHARACTERIZATION OF SURFACE FUNCTIONALITY OF COALS BY PHOTOACOUSTIC FTIR SPECTROSCOPY, REFLECTANCE INFRARED MICROSPECTROMETRY, SCANNING ELECTRON MICROSCOPY/SECONDARY ION MASS SPECTROMETRY, AND X-RAY PHOTOELECTRON SPECTROSCOPY, BY Brian M. Lynch, J. Anthony MacPhee, and Ronald R. Martin, to be published in the Proceedings of the 1987 International Conference on Coal Science, October 1987.

1.

PHOTOACOUSTIC FTIR SPECTROSCOPY IN DETECTION OF COAL OXIDATION,

by
Brian M. Lynch and J. Anthony MacPhee.
Chapter 4 of
"Chemistry of Coal Weathering",
Edited by Charles R. Nelson. Elsevier Publishers, Amsterdam.

Chapter 4

PHOTOACOUSTIC FTIR SPECTROSCOPY IN DETECTION OF COAL OXIDATION

BRIAN M. LYNCH
Department of Chemistry, St. Francis Xavier University,
Antigonish, Nova Scotia B2G 1C0 (Canada)
and
J. ANTHONY MacPHEE
Energy Research Laboratories
Canada Centre for Mineral and Energy Technology
(Energy, Mines, and Resources Canada)
Ottawa, Ontario K1A 0G1 (Canada)

Table of Contents

Section	Page
1. Photoacoustic FTIR Spectroscopy	1
2. Photoacoustic FTIR Spectrosccopy of Coals	
(a) Introduction	2
(b) Experimental Details of Acquisition of Spectra	4
(c) Preparation of Coal Samples for Spectroscopy	5
3. Studies of Coal Oxidation by Photoacoustic FTIR Spectroscopy	
(a) Naturally Weathered Coals	6
(b) Oxidations below 100°C at Atmospheric Pressure	8
(c) Oxidations between 100-200°C	9
(d) Oxidations above 200°C	10
4. Enhanced Detectability of Added Peroxygen Species in Coals by Chemical Procedures	12
5. Thermal Deceomposition Pathways for Surface Peroxide Species of Exposed Coals	16
6. Correlations of Photoacoustic FTIR Spectra of Oxidized Coals with Technological Properties	19
CONCLUSIONS	21
ACKNOWLEDGEMENTS	21
REFERENCES	22

1. PHOTOACOUSTIC FTIR SPECTROSCOPY

The photoacoustic phenomenon was discovered by Alexander Graham Bell over one hundred years ago (1). When a gas occupying a sealed compartment was illuminated with pulsed radiation, pressure fluctuations (sound waves) were detected by a sensitive microphone inside the compartment.

Application of this observation to modern infrared measurements on solids was first suggested by Rosencwaig (2,3), and in current systems, a microphone is used to detect pressure fluctuations resulting from pulsed infrared source radiation modulated by the interferometer of a Fourier Transform infrared spectrometer. Absorption of infrared radiation incident on a solid heats its surface, which in turn heats a boundary layer of gas surrounding the sample. The modulated radiation produces expansion and contraction of the boundary layer, detected by the microphone as sound in the form of a photoacoustic interferogram. The depth of the interaction between radiation and sample depends upon the thermal conductivity and heat capacity of the sample and of the carrier gas, the degree of subdivision of the sample, and the modulating frequency of the incident radiation.

An excellent review of the advantages and limitations of the technique has been given by J. F. McClelland (4).

For best results, modulated frequencies should be kept in the low audio range where microphones are most sensitive; appropriate interferometer moving mirror velocities are below 0.1 cm s^{-1}. Systematic variation of the interferometer moving mirror velocity (and thus the modulating frequency) provides depth profiling information (5). Single-beam photoacoustic spectra are usually referenced to a highly absorbing background spectrum obtained using carbon black, when the resultant photoacoustic infrared Fourier Transform (PAIFT) spectrum resembles the conventional absorbance spectrum of the sample, but there are several caveats governing the acquisition of high-quality spectra.

The acoustic character of the acquired signal requires highly efficient acoustic isolation and vibrational isolation of the microphonic detector system from its surroundings. For those FTIR instruments with acoustically "rough" interferometers, this may negate the possibility of obtaining high-quality spectra with reasonable acquisition times (i.e., comparable to those for a conventional transmission spectrum). Also, an intense photoacoustic signal arises from dilute water vapor, so that

unless both sample and transducing gas are rigorously dried, artefactual components from the rotation-vibration features of the infrared signals from water vapor appear in the transformed spectrum.
Finally, since the infrared source intensity determines the photoacoustic signal response, frequent "normalization" of the reference response of the carbon black is desirable.

2.PHOTOACOUSTIC FTIR SPECTROSCOPY OF COALS:

(a) INTRODUCTION

Although sensitivity enhancements in vibrational spectroscopy accompanying the FT mode of data acquisition might be expected to assist with specific characterization and analysis of functional groups in coals and in detection and quantitation of chemical transformations, few truly new insights into coal oxidation have resulted from these enhancements, and the results are of limited technological significance. For example, the recorded sensitivity of KBr-pellet FTIR spectroscopy in detecting oxidative deterioration in coals is much less than that of standard plasticity tests. Painter and his colleagues (6) at Pennsylvania State University found less than a 1 % increase in the ratioed intensity of carbonyl bands for bituminous coals oxidized at 60^{o}C or 140^{o}C for periods sufficient to decrease maximum Gieseler fluidity by over 90 %, and Huggins, Huffman, and co-workers (7) at the U. S. Steel Corporation found that diffuse reflectance infrared Fourier Transform (DRIFT) spectroscopy was an insensitive indicator of oxidation for Appalachian bituminous coals.

The relatively disappointing performance of these two FTIR techniques in detecting and correlating the changes in plastic properties may be accounted for in terms of the surface-controlled nature of the fusing together of coal particles, which is likely to be highly sensitive to oxidative alteration of very thin surface layers.
The surface-dominated nature of the photoacoustic response process, coupled with the signal/noise enhancements of Fourier Transform infrared instrumentation, suggested to us in 1980 that this technique could have substantial advantages for the study of coals over more conventional FTIR methods.

A priori, the expected advantages are:
intensely absorbing samples give the most intense photoacoustic response (the converse of transmission-FTIR with coals);
minimal sample preparation is required;
the photoacoustic response is relatively insensitive to the degree of subdivision of the sample particles;
although more finely divided particles have greater surface/volume ratio, the surrounding free space occupied by the transducing gas decreases with decreasing particle size;
the ability to observe surface features generated by chemical transformations.
Rockley and Devlin (8) were the first to obtain PAIFT spectra of coal surfaces. They suggested that effects of both oxidation and abrasion were clearly apparent. The group at St. Francis Xavier University (9) monitored the surface and bulk air-oxidation of coals at 120°C - 150°C by PAIFT spectroscopy and the preliminary results suggested generation of a variety of carbonyl absorptions, including ketones, carboxylic acids, and carboxylic acid anhydrides. Generally similar results have been reported more recently by McClelland and co-workers (10) and by Zerlia (11). Over the last six years, we have developed a series of applications to coals which we review in this chapter.

In practice, we have found that PAIFT spectra of coals do not exhibit the sloping baselines characteristic of alkali halide pellet spectra (contrast a recent report of such FTIR spectra of Canadian coals (12)), and subtraction to yield difference spectra revealing introduced features is straightforward and avoids arbitrary scaling procedures.
A representative example is reproduced in Figure 1.

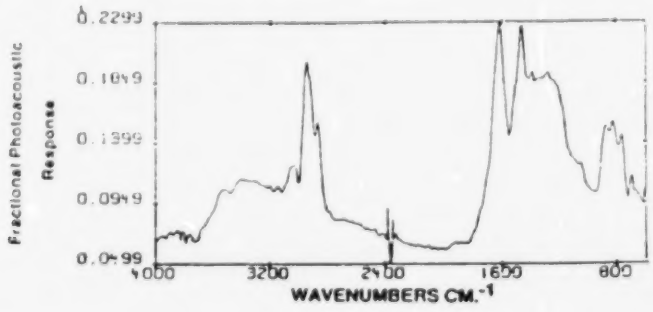


Figure 1
Typical PAIFT Spectra of
Cape Breton Island Bituminous Coal # P-303

(b) EXPERIMENTAL DETAILS OF ACQUISITION OF SPECTRA

The PAIFT Spectra reproduced in the accompanying Figures were obtained using a Bruker IFS110 purge-type Infrared Fourier System with a germanium on potassium bromide beamsplitter. The interferometer compartment of the spectrometer was insulated acoustically from the sample compartment using a box fabricated from expanded polystyrene. Modulated source radiation was reflected into a E G & G Princeton Applied Research Model 6003 Photoacoustic accessory fitted with a zinc selenide window and the amplified photoacoustic output was transmitted to the data system of the IFS110. The nitrogen purge flow was interrupted during scanning. In the standard operating mode, 10-50 mg of the dried coal were placed in the sample cup, and 128 photoacoustic interferograms were collected at 8 $cm.^{-1}$ resolution with a zero-filling factor of 2, corresponding to final transformed spectra encoded every 4 $cm.^{-1}$. The photoacoustic spectra were obtained by ratioing against the energy output (black-body response) from a similarly dried sample of Fisher Carbon Lampblack C-198. Displayed spectra are smoothed using a five-point Golay-Savitzky algorithm. The interferometer mirror velocity was 0.08333 $cm\ s^{-1}$, and spectra were acquired from 4000 to 400 $cm.^{-1}$.

Difference spectra were obtained by least-squares subtraction, i.e.-

$$\text{Difference intensity} = \text{(spectrum of treated coal)} - x\ \text{(spectrum of untreated coal)}$$

where x is the subtraction coefficient. Subtractions were effected on the digitized spectra under the control of the ATS85 instrument software package on a Bruker Aspect 2000 computer. Sets of individual spectra of different portions of the coal samples (generally four to six per set) gave matching spectra (i.e. zero baseline over the ranges used for subtractions (2000-1400 $cm.^{-1}$ for the chemically treated samples or 2000-1500 $cm.^{-1}$ for samples subjected to high-pressure oxidations)).
The subtraction coefficients x were in the range 0.99-1.01.
Illustrated difference spectra in the various Figures were obtained by least-squares subtraction. The smoothing algorithm was applied to these difference spectra.

(c) PREPARATION OF COAL SAMPLES FOR SPECTROSCOPY

As-received coals were ground to the range 50-60 mesh under liquid nitrogen using a Brinkmann Pulverizer, and were dried at 100°C under vacuum for 6 h before transfer to the sample cup of the photoacoustic accessory. Oxidations at atmospheric pressure were effected in conventional Fisher IsoTemp Ovens, or by irradiation under a 300W Photoflood lamp (samples were placed approximately 10 cm from the lamp, providing a surface temperature of approximately 75°C).

For the high-pressure oxidations, the coals were ground and sized to 50 mesh and oxidized by dry air at 55°C and 9 MPa for periods ranging from 3 to 196 h. All samples were subsequently subjected to the standard drying procedure before PAIFT spectroscopic examination.

Analytical and fluidity data on the as-received coal samples subjected to the high-pressure oxidations are presented in Table 1.

Table 1

Coal Samples Subjected to High-Pressure Oxidations

Analytical and Fluidity Data on Fresh Coals

Coal Designation	Classification	C, %	H, %	O, %	Gieseler Fluidity (dd/min)
Fording (Western Canadian)	HV 'A'	80.49	5.07	5.60	365
Greenhills (Western Canadian)	HV 'A'	81.56	4.75	4.79	24
Alto (Appalachian, U. S. A.)	HV 'A'	79.69	5.20	7.47	1580
Barton (U. S. A.)	HV 'A'	81.81	5.08	4.34	20350
McClure (U. S. A.)	MV-HV 'A'	83.07	4.74	3.82	7900
Basset (U. S. A.)	L-MV	85.01	4.42	3.20	32

3. STUDIES OF COAL OXIDATIONS BY PHOTOACOUSTIC FTIR SPECTROSCOPY

(a) Naturally Weathered Coals

PAIFT spectroscopy is capable of differentiating among naturally weathered coal samples. The samples were as-mined Appalachian bituminous coals from the Phalen Seam, Cape Breton Island, Nova Scotia, taken 0, 3, 15, 18, and 24 metres from an exposed surface.

The oxygen contents (direct determination) of these samples are as listed in Table 2. The relative integrated intensities (normalized for the most deeply immersed coal) over the 1600-1800 cm.-1 region of the PAIFT spectra are used as an indexing factor for the extent of oxidation.

Table 2

Naturally Weathered Coals

Coal Designation	Distance (m)	Oxygen, %	PAIFT Intensity
P-309	0	8.34	1.415
P-310	3	7.34	1.244
P-314	15	7.01	1.118
P-315	18	6.79	1.094
P-317	24	6.22	1.000

Figure 2 illustrates that the integrated PAIFT spectral intensity over the region 1600-1800 cm.$^{-1}$, normalized to the peak intensity at 1600 cm.$^{-1}$ for the most deeply embedded coal, is a linear function of the analyzed oxygen

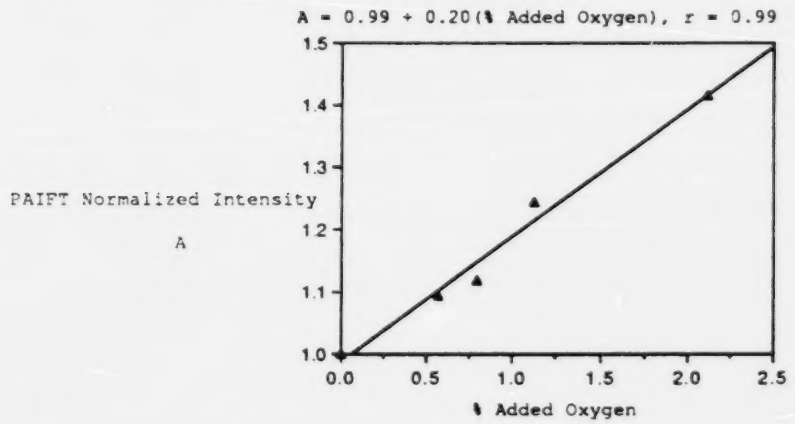


Figure 2
PAIFT Intensity/Oxygen Correlation,
Naturally Weathered Coals

We have also examined the possibilities of differentiating between maceral concentrates derived from a series of U. K. coals in terms of the association of the asymmetry of the "1600 cm.-1 band" of these coals with their intrinsic oxygen contents. This was done by normalizing the maximal peak intensity and comparing the integrated areas in the 1600-1800 cm.-1 region with the percentage of oxygen.

The maceral concentrates (vitrinites) were obtained from Dr. J. Allan of Esso Resources, Calgary.

Table 3

Vitrinite Concentrates

Vitrinite Code #	Oxygen, %	PAIFT Intensity, 1600-1800cm.-1
V8	8.30	1.000
V7	10.1	1.086
V6	10.5	1.040
V3	15.9	1.170
V4	16.3	1.176
V2	17.2	1.216
V1	17.5	1.277

Figures 3 and 4 illustrate correlation of the photoacoustic infrared intensity with the oxygen contents.

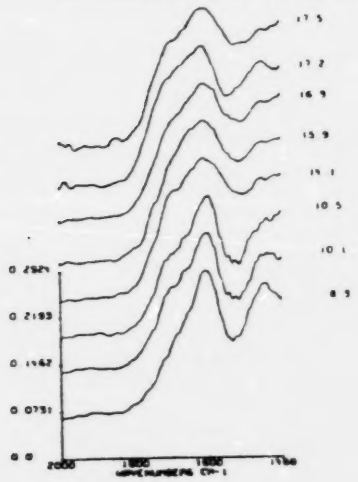


Figure 3
PAIFT 1600-1800 cm.$^{-1}$
Intensity for Vitrinite Concentrates

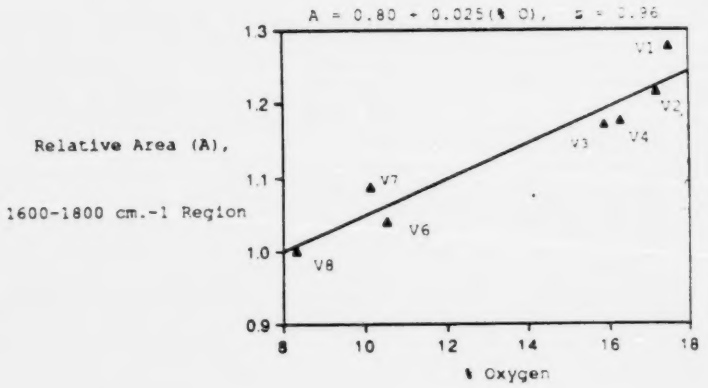


Figure 4
Correlation of PAIFT Area with Oxygen Content,
Vitrinite Concentrates

(b) Oxidations below 100°C at atmospheric pressure

In these experiments, we simulated natural oxidation of coals in sunlight by exposing finely powdered coal samples to irradiation under a 300W Photoflood lamp; samples were placed approximately 10 cm from the lamp, providing a surface temperature of approximately 75°C.

As a representative example, consider the oxidation of Harmer seam bituminous coal (a British Columbia coal): Figure 5 shows progressive changes occurring for such exposure to 200 h, and difference spectra are shown in Figure 6. Changes are detectable after 20 h exposure, and the growth pattern of the carbonyl peak area is illustrated as Figure 7.

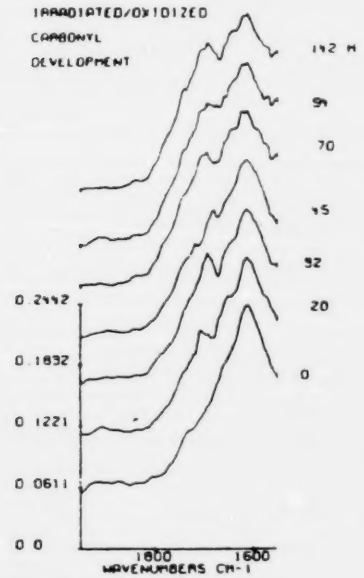


Figure 5
Progressive Changes in Spectra
of Oxidizing Harmer Coal

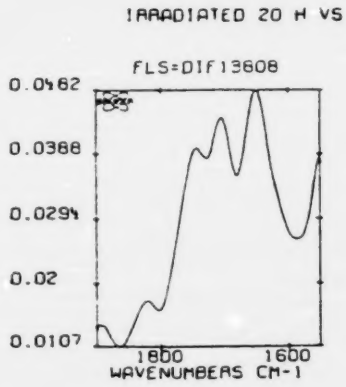


Figure 6
Difference Spectra, Oxidizing Harmer Coal

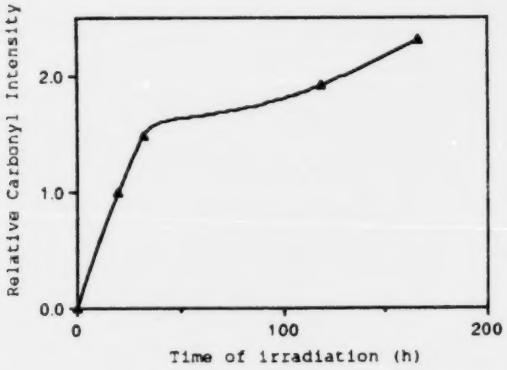


Figure 7
Growth Pattern of Carbonyl Peak Development,
Oxidizing Harmer Coal

(c) Oxidations between 100-200°C

Quantitative methylations of bituminous coals using phase-transfer catalyzed processes based upon those developed by Liotta and coworkers (13-15) have been shown to enhance the resolvability of the features associated with the introduction of various types of additional carbonyl-type oxygens (16).

The enhanced resolvability may be termed "chemical deconvolution". The two accompanying Figures (8 and 9) illustrate this for a British Columbia bituminous coal (Harmer Seam) oxidized in air at 110°C for 336 h, and for the stages of oxidation of a Cape Breton Island bituminous coal oxidized at 122°C for up to 400 hours.

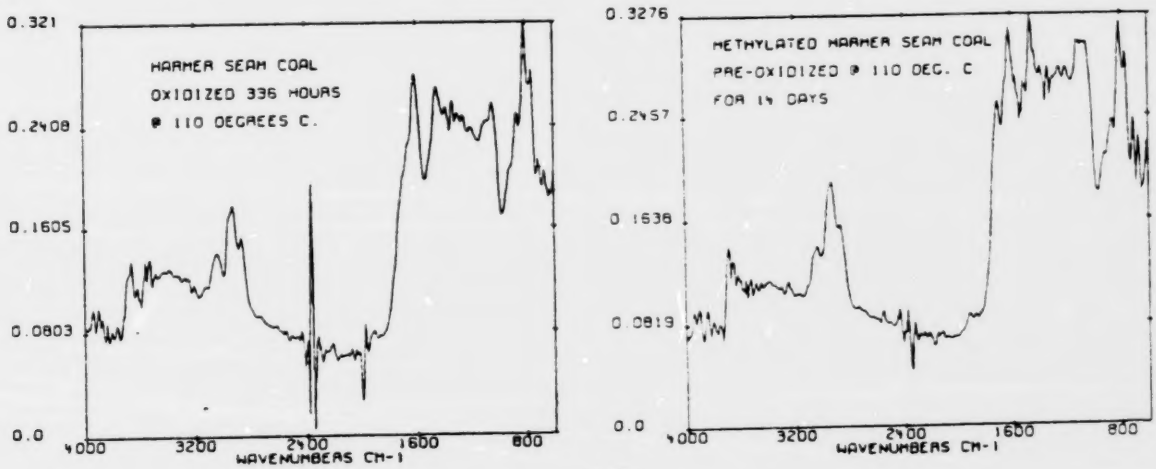


Figure 8
PAIFT Spectra of Harmer Coal oxidized 336 h at 110°C and of Product of Quantitative Methylation

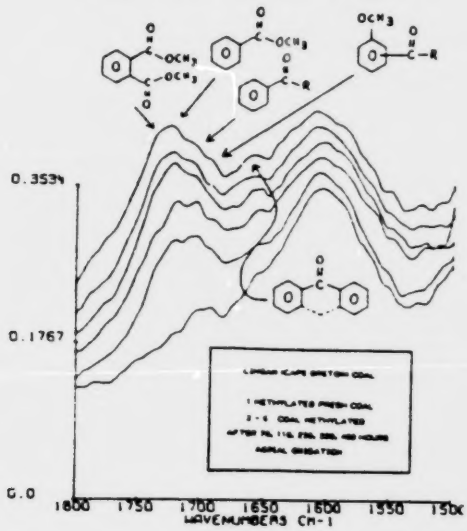


Figure 9
Resolvable features in Methylation products from Cape Breton Island bituminous coal oxidized at 122°C for 0-400 h

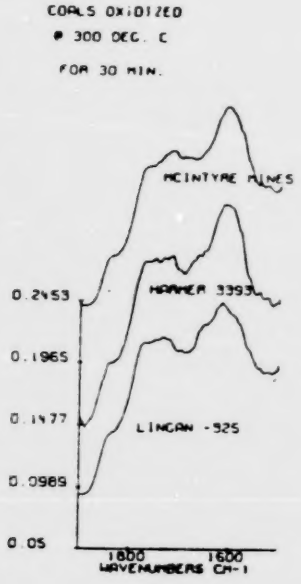
The methylation processes involve initial formation of anionic centres by deprotonation of acidic oxygen functions, effected by treatment with tetra-n-butylammonium hydroxide in aqueous tetrahydrofuran under nitrogen, followed by S_N2 reaction with iodomethane, as in:

$$COAL.OH + NBu_4^+ + OH^- \longrightarrow COAL.O^- + NBu_4^+ + H_2O$$

$$COAL.O^- + CH_3.I \longrightarrow COAL.O.CH_3$$

(d) Oxidations above 200°C

Fuller and his colleagues (17) and Griffiths and his colleagues (18) employed DRIFT spectroscopy to follow the course of oxidations of bituminous coals for brief periods at temperatures as high as 300°C. Fuller's group proposed that aryl carbonates are formed, while Griffiths suggested that aromatic acid anhydrides are generated. PAIFT spectroscopy of three typical Canadian bituminous coals, oxidized in air at 300°C for 30 min, and of their products of chemical modification, support Griffiths' suggestion. Thus, Figure 10 reveals that the carbonyl regions of the oxidized coals show resolvable absorptions around 1760 and 1820 $cm.^{-1}$, which after alkaline hydrolysis and washing, lose any carbonyl absorptions (Figure 11).



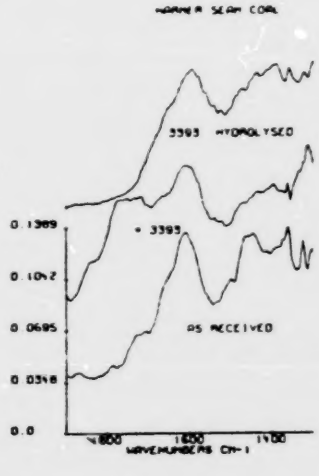


Figure 10: Carbonyl Regions, Coals Oxidized at 300°C
Figure 11: Salt Formation from Coals of Figure 11

The results suggest occurrence of the reaction type:

$$o\text{-}C_6H_4.(CO)_2O \quad \text{-- } (OH^-) \text{->} \quad o\text{-}C_6H_4(CO_2^-)_2$$

Consistent with this suggestion is the observation that after phase-transfer methylation of the oxidized coals, products are formed whose PAIFT spectra (Figure 12) exhibit carbonyl frequencies indicative of vicinal methoxycarbonyl groups, i.e:

$$o\text{-}C_6H_4(CO_2H)_2 \text{ -----}(Bu_4N^+OH^-/MeI)\text{---> } o\text{-}C_6H_4(CO_2Me)_2$$

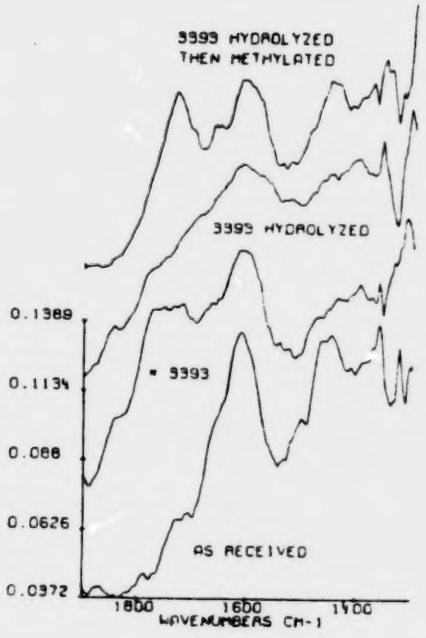


Figure 12: Methoxycarbonyl Features in Methyl Derivatives of Coals of Figure 10

4. ENHANCED DETECTABILITY OF ADDED PEROXYGEN SPECIES IN COALS BY CHEMICAL PROCEDURES - Generation of Carbonyl Functionality from Base-Promoted Decomposition Reactions

As indicated in section 3. (c), we have used quantitative methylations of bituminous coals phase-transfer catalyzed processes based upon those developed by Liotta and coworkers (13-15).

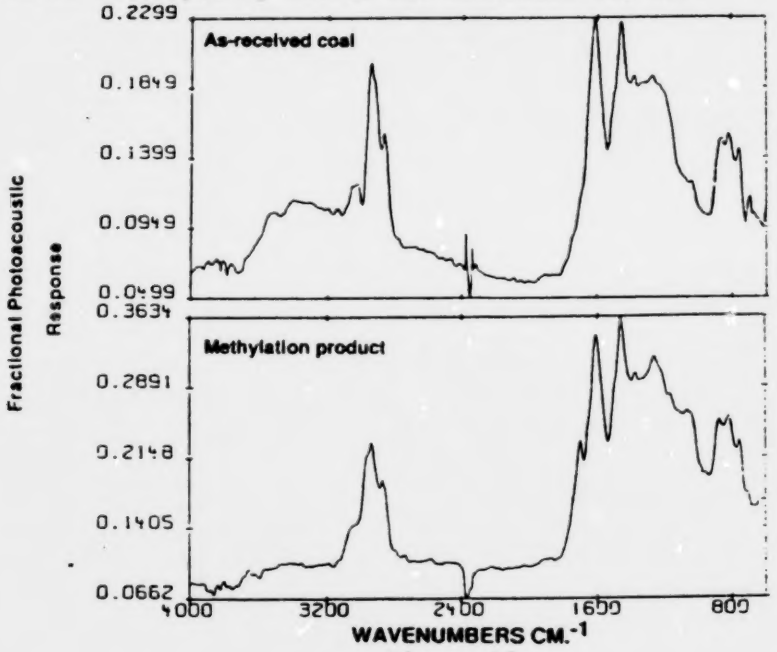
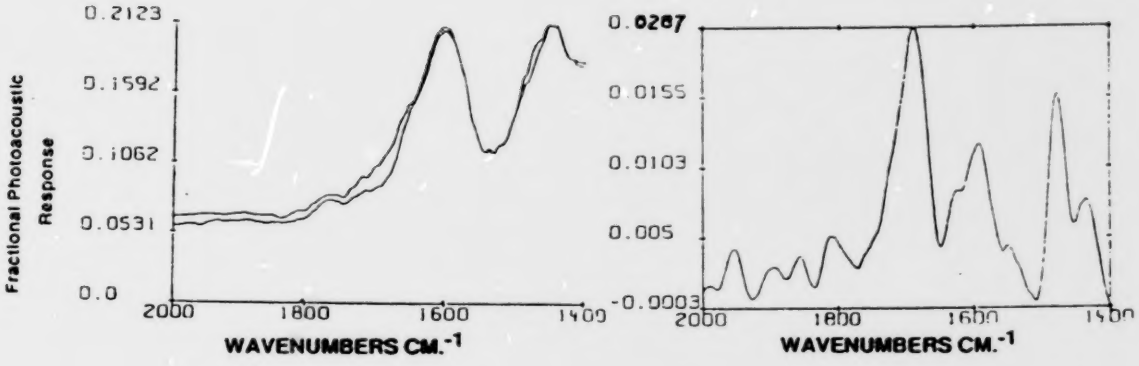


Figure 13
Typical PAIFT Spectra of Cape Breton Island
Bituminous Coal # P-303
and of its Product of Quantitative Methylation

Figure 13 reproduces PAIFT spectra for a typical sample of freshly ground, newly mined bituminous coal from Cape Breton Island, Nova Scotia, Canada, and of its product of quantitative methylation. Noteworthy features in the methylation product are the horizontal baseline patterns and the absence of O-H absorptions. In previously reported work (16) we remark that many such methylated coals exhibit distinct carbonyl absorption in the 1680-1705 $cm.^{-1}$ region, absent from the original coal.

Although such results could be explained by a high-frequency shift of a pre-existing carbonyl species caused by removal of inter-group hydrogen-bonding interactions, more detailed examinations show that the new carbonyl species arise **irreversibly** at the stage of coal anion formation, before the methylation step: the overlay spectrum of Figure 14 illustrates this point. The new peak is unaffected by reacidification of the reaction mixture and thus cannot involve displacement of a carboxylate:carboxylic acid ratio.



Figures 14, 15
Overlay and Difference Spectra of the Coal of Figures 1 and 13, before and after Coal Anion Generation

The overlay spectrum (Figure 14) for the coal of Figure 13 and the corresponding reprotonated "coal anion" (re-acidified and thoroughly washed) indicates asymmetry between 1600-1700 cm.-1, and the difference spectrum of Figure 15 reveals a simple carbonyl peak with maximum at 1686 cm.-1, which we classify as an aralkyl ketone.

Chemical confirmation of assignment as a ketone is provided by reduction of the base-treated coal by tetrabutylammonium borohydride in aqueous tetrahydrofuran, eliminating the carbonyl absorption peak. Acetylation of the reduction product (involving heating under reflux with an acetic anhydride/pyridine mixture) leads to an acetylated species with identifiable alcoholic acetate absorption at 1736 $cm.^{-1}$, in addition to the principal phenolic acetate features around 1760-1765 $cm.^{-1}$.

The reactions effected are:

$$COAL.C{:}O.R \quad ---(NBu_4^+\ BH_4^-,\ THF/H_2O) ----> \quad COAL.CH.(OH).R$$

$$COAL.CH.(OH).R \ ----((CH_3.CO)_2O,\ C_5H_5N) \ ---> \ COAL.CH.(O.CO.CH_3).R$$

It is well documented (see, e.g., (19)) that borohydride ion reductions are specific for ketone --> alcohol conversions, without affecting carboxylic acid functions.

We attribute formation of these new absorbing entities to base-promoted decompositions of peroxide species, that is:

$$COAL.CHR.O.O.R' + OH^- \text{-----> } COAL.C{:}O.R + R'O^- + H_2O$$

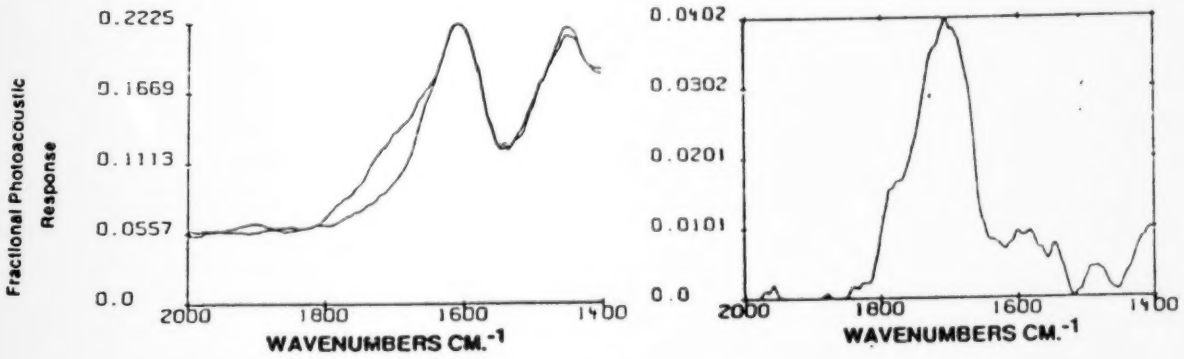
(R = alkyl or aralkyl, R' = H, alkyl, or aralkyl)

Such reactions for simple organic peroxides are well documented (20-22), but their possible relevance to coal transformations has not been recognized previously. Although it is generally accepted (23,24) that peroxy species are generated in the initial stages of oxidation of bituminous coals at moderate temperatures, the major supporting evidence derives from non-spectroscopic studies (25-28).

Our results (for previous reports, see Lynch and co-workers (29,30)) are the first **spectroscopic evidence** supporting the postulated intermediacy of peroxides for coals oxidized by simple aerial exposure at routine laboratory temperatures.

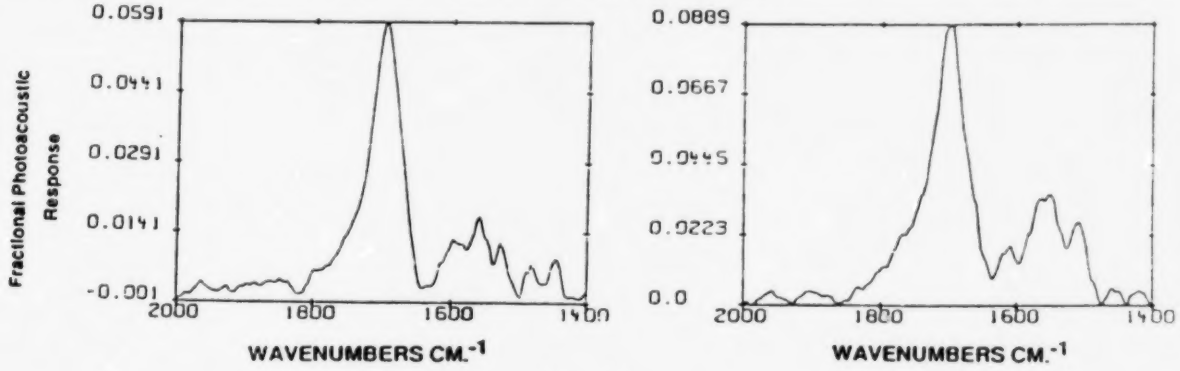
As far as we are aware, all previous FTIR studies of coal oxidations where development of carbonyl absorptions has been detected refer to oxidations at 100°C or above (see references 11,12, 31-36).

Note that the overlay and the difference spectra reproduced as Figures 14 and 15 bear a general resemblance to patterns for the same coal oxidized intentionally at higher temperature (shown as Figures 16 and 17), but the carbonyl-region band envelopes are distinctly different; the carbonyl-region absorption in Figure 16 obviously possesses multiple, unresolved, contributing features.



Figures 16, 17
Overlay PAIFT Spectra of the Coal of Figures 1 and 13
revealing changes after Thermal Oxidation in Air at 105°C for 24 h,
and Corresponding Difference Spectrum

The intensities of the ketone carbonyl peaks in the difference spectra derived from base-treatment of the same coal after storage in the laboratory at about 20°C for six and for twelve months increase progressively without significant increase in band complexity (see Figures 18 and 19): "freshly prepared" coal, 0.020 intensity units; after six months, 0.059; after twelve months, 0.089.



Figures 18, 19
PAIFT Difference Spectra for Coal of Figure 1
stored at 20°C for six months (Figure 18)
and for twelve months (Figure 19)

Occurrence of base-promoted decomposition of peroxide species generated at the coal surfaces, analogous to those we propose, explains Ignasiak, Szladow, and Montgomery's observed restoration (37) of the large dilatation of slightly oxidized high-volatile bituminous coals by treatment with aqueous barium hydroxide.

If the original coal sample of Figure 13 is derivatized through quantitative acetylation, added ketone-type carbonyl species derived from the coal itself are not formed (see Figure 20). Under these conditions, superficial peroxides transfer oxygen to the pyridine solvent yielding pyridine 1-oxide.

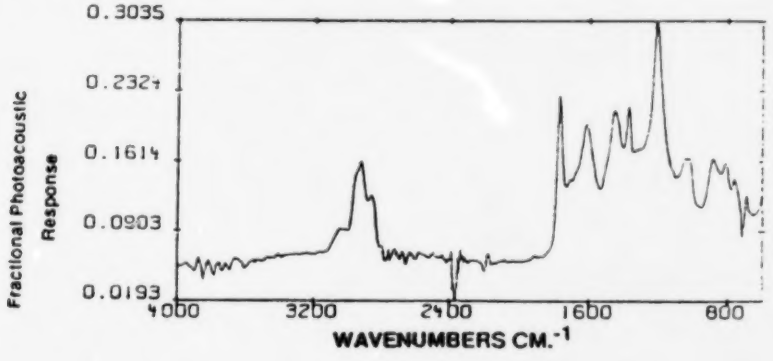


Figure 20
PAIFT Spectrum, Quantitatively Acetylated Coal of Figure 1

5. THERMAL DECOMPOSITION PATHWAYS FOR SURFACE PEROXIDE SPECIES OF EXPOSED COALS

We have been able to compress the time scale of oxidative changes by subjecting powdered bituminous coals to pressurized air at slightly elevated temperatures. With such samples, we observe distinct, readily differentiated types of carbonyl absorptions (around 1750, 1720, 1690, and 1650 $cm.^{-1}$) whose relative proportions are different for different coals, and we propose that the carbonyl species are generated by the standard vacuum drying procedure from thermal decomposition of the assumed peroxide species, and have escaped previous detection since the grinding procedures associated with sample preparation for KBr-pellet transmission FTIR- and Diffuse Reflectance FTIR-spectroscopic measurements impose randomization and dilution of surface infrared absorbing groups.

Representative difference spectra taken for the six coals of Table 1 at the stage of 48 hours oxidation are illustrated in Figures 21 through 26, and are summarized in bar-graphical form in Figure 27.

These peaks are proposed to arise from specific decompositions of peroxides occupying different, isolated, structural sites in the coals. The 1750 $cm.^{-1}$ and 1720 $cm.^{-1}$ peaks are attributed to decompositions of α-hydroperoxyethers to yield cyclic or open-chain esters; the 1750 $cm.^{-1}$ (lactone species) from a cyclic ether precursor, and the 1720 $cm.^{-1}$ from an open-chain precursor, that is:

$$Ar.CH_2.O.R \xrightarrow{(O_2,\ 55^{\circ}C,\ 9\ MPa)} Ar.CH(O.O.H).O.R$$

$$Ar.CH(O.O.H).O.R \xrightarrow{(100^{\circ}C,\ vacuum)} Ar\ CO.O.R$$

Stock and Wang (38) have recently postulated generation of lactone species from the ruthenium (VIII)-catalyzed oxidation of Illinois No. 6 bituminous coal by sodium periodate.

The 1690 and 1650 $cm.^{-1}$ peaks are attributed to decompositions of α-hydroperoxy aralkanes or of hydroperoxy diarylalkanes, that is:

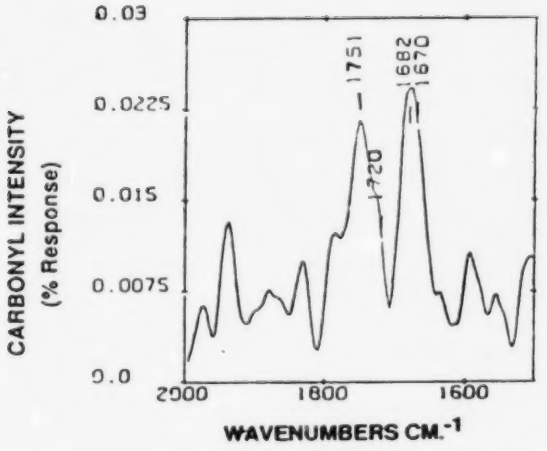
$$Ar.CH_2.R \xrightarrow{(O_2,\ 55^{\circ}C,\ 9\ MPa)} Ar.CH(O.OH)R$$

$$Ar.CH(O.OH)R \xrightarrow{(100^{\circ}C,\ vacuum)} Ar.CO.R$$

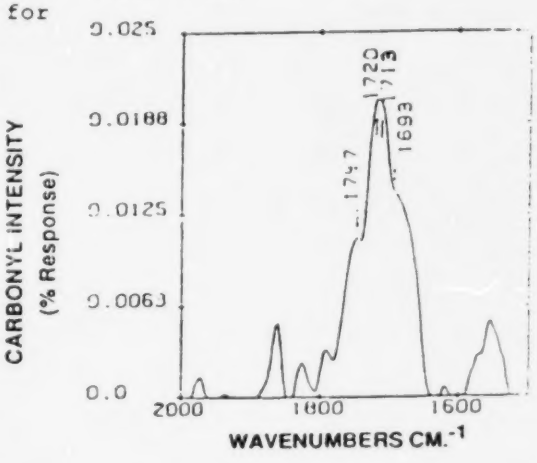
$$Ar.CH_2.Ar \xrightarrow{(O_2,\ 55^{\circ}C,\ 9\ MPa)} Ar.CH(O.OH)Ar$$

$$Ar.CH(O.OH)Ar \xrightarrow{(100^{\circ}C,\ vacuum)} Ar.CO.Ar$$

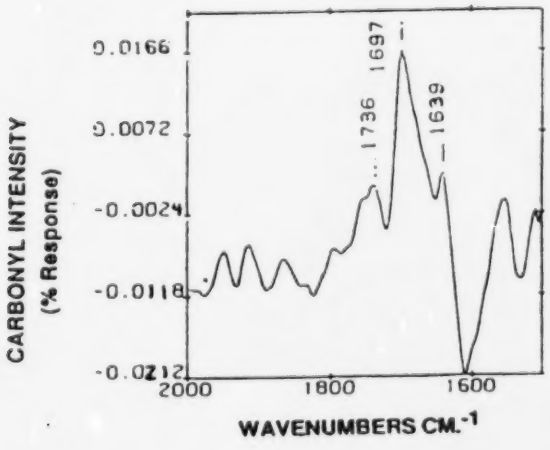
Figures 21-26
PAIFT Difference Spectra,
(Oxidized 48 h) - (Fresh Coal)
for



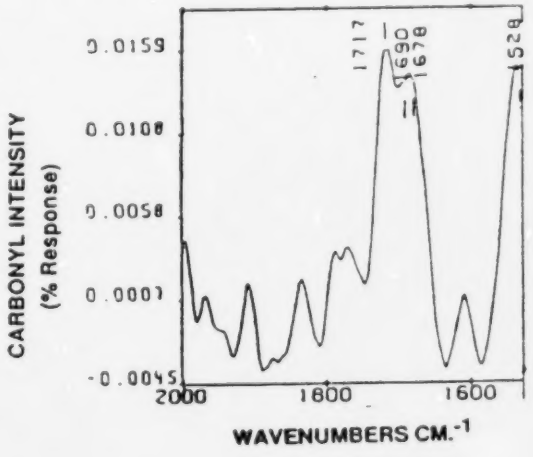
Fording Coal (Figure 21)



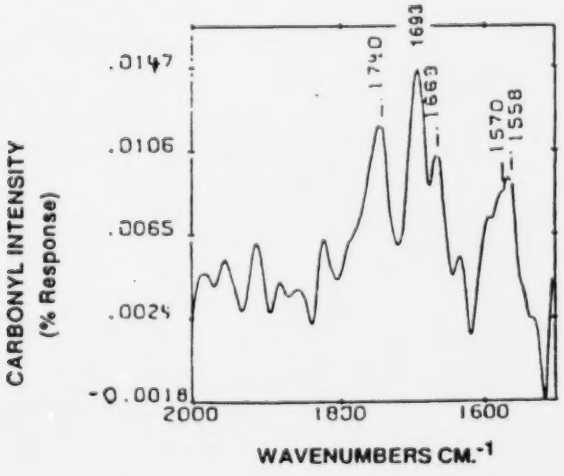
Greenhills Coal (Figure 22)



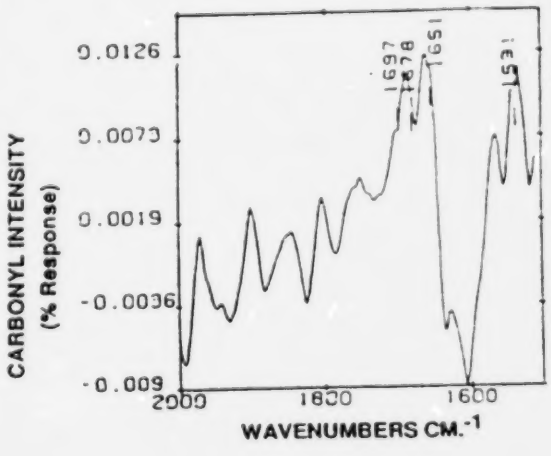
Alto Coal (Figure 23)



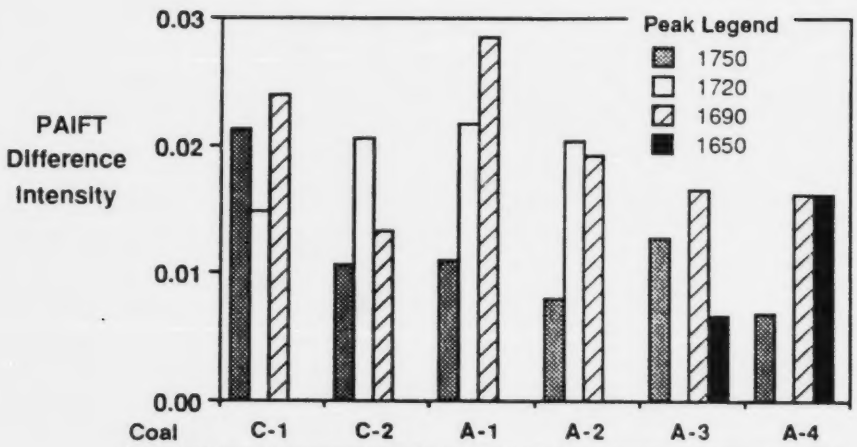
Barton Coal (Figure 24)



McClure Coal (Figure 25)



Basset Coal (Figure 26)



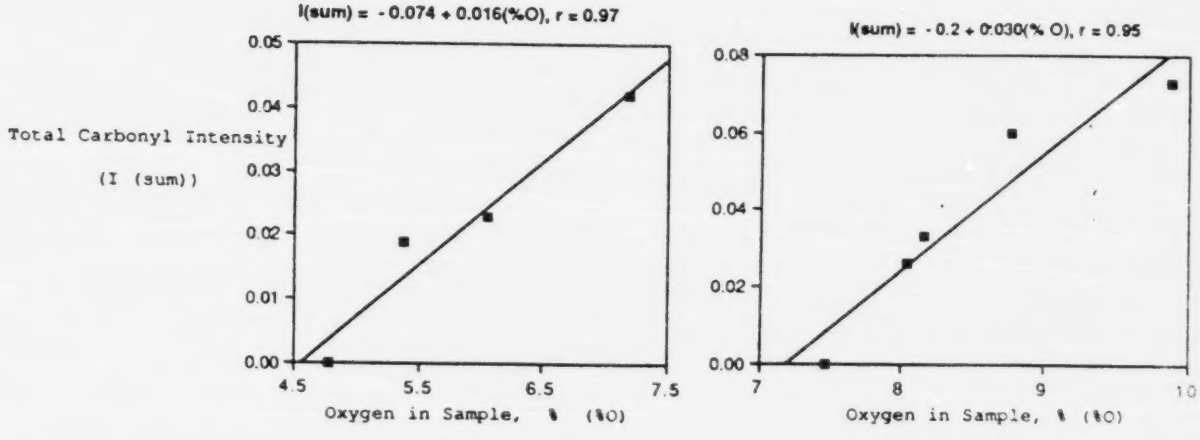
Distribution of Carbonyl Peak Intensities for 6 coals oxidized for 48 h

C-1: Fording; C-2: Greenhills; A-1, Alto; A-2, Barton; A-3, McClure; A-4, Basset

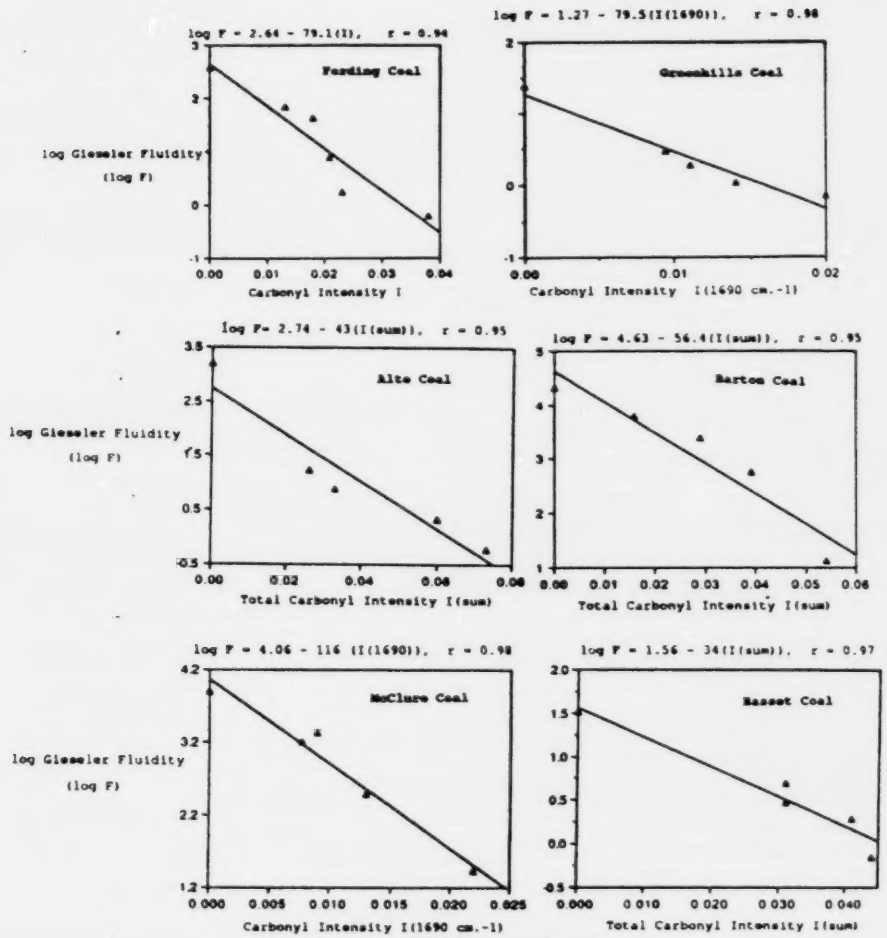
Figure 27

6. CORRELATIONS OF PHOTOACOUSTIC FTIR SPECTRA OF OXIDIZED COALS WITH TECHNOLOGICAL PROPERTIES

The relative intensities of the thermally generated carbonyl absorptions for the six coals we have examined are dependent in a complex manner upon oxygen content, carbon/hydrogen ratio, and the progress of oxidation, but there are general quantitative associations of increasing carbonyl intensities with many characteristics of the behavior of the sequences of oxidized samples for a given coal. These include relationships between thermally developed carbonyl intensity and oxygen content for the Greenhills coal (Western Canadian: bituminous high-volatile 'A') and for the Alto coal (Appalachian U. S. bituminous high-volatile 'A')(Figures 28, 29), and carbonyl intensity and Gieseler fluidity for the Fording and Greenhills (Western Canadian: bituminous high-volatile 'A') coals, and also for the four U.S. coals, illustrated in Figures 30 through 35. There is also a positive, quantitative, correlation between the initial oxygen content of the coal samples and the "snapshot" of developed carbonyl intensity after 48 h oxidation (Figure 36).



Figures 28, 29
Carbonyl Intensity (PAIFT Spectra) vs. Oxygen %
for Greenhills (Figure 28) and Alto (Figure 29) Coals


log F = 2.64 - 79.1(I), r = 0.94
Fording Coal
log Gieseler Fluidity
(log F)
Carbonyl Intensity I
log F = 1.27 - 79.5(I(1690)), r = 0.98
Greenhills Coal
Carbonyl Intensity I(1690 cm.-1)
log F= 2.74 - 43(I(sum)), r = 0.95
Alto Coal
log Gieseler Fluidity
(log F)
Total Carbonyl Intensity I(sum)
log F = 4.63 - 56.4(I(sum)), r = 0.95
Barton Coal
Total Carbonyl Intensity I(sum)
log F = 4.06 - 116 (I(1690)), r = 0.98
McClure Coal
log Gieseler Fluidity
(log F)
Carbonyl Intensity I(1690 cm.-1)
log F = 1.56 - 34(I(sum)), r = 0.97
Basset Coal
Total Carbonyl Intensity I(sum)

Figures 30-35
log Fluidity vs. Carbonyl Intensity Relationships
for
Fording Coal (Figure 30)
Greenhills Coal (Figure 31)
Alto Coal (Figure 32)
Barton Coal (Figure 33)
McClure Coal (Figure 34)
Basset Coal (Figure 35)

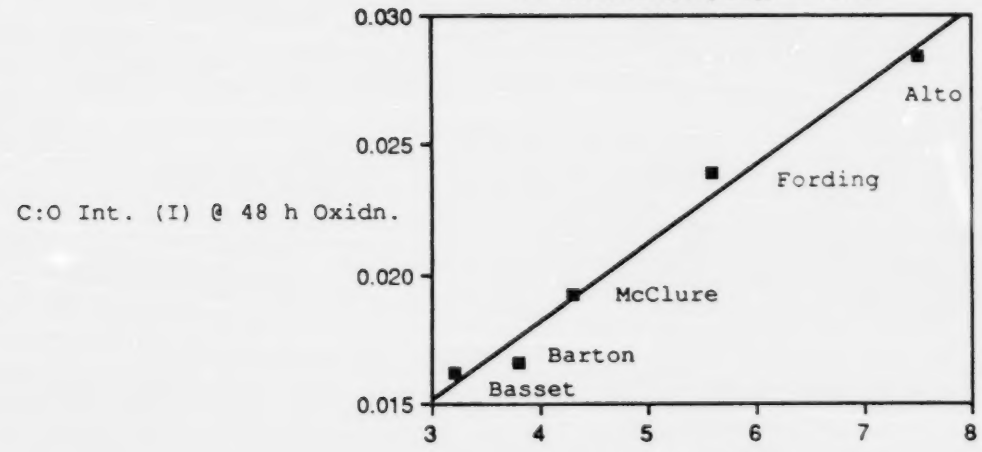


Figure 36
Correlation of Developed Carbonyl Intensity
with Initial Oxygen Content for All Coals

However, the coals are behaving in sufficiently different fashions (both in the quantitative distribution of the various introduced carbonyl species, in the their qualitative rates of generation, and in the nature of the influence of changed functionality on the technical properties) that generalized treatment as a single data set would obscure the individual correlations. In view of our findings, we suggest that extreme caution would be appropriate in using the approaches adopted by Fredericks and his co-workers (39), where attempts are made to make generalized predictions of technological properties using principal factor analyses of FTIR spectra of a wide range of coals.

CONCLUSIONS

We have indicated the potential for surface characterization of coals by PAIFT spectroscopy. We suggest that the evidence presented above for previously unquantified and undetected peroxide species on coal surfaces requires further consideration of the influence of the proportion of surface peroxides upon the course(s) of coal pyrolyses, and provides strong support to recent proposals (40) recommending storage of laboratory samples of coals in sealed ampoules.

ACKNOWLEDGEMENTS

The research work upon which this paper is based was supported by Energy, Mines, and Resources Canada through the Department of Supply and Services, Contract Serial Numbers OST83-00347 and OST85-00235, and under Research Agreements Nos. 230 (1985-1986) and 189 (1986-1987). We thank Drs. J. S. Gethner and R. Liotta (Exxon Research and Engineering Company) and Dr. R. A. Durie (R. W. Miller Holdings, Sydney, Australia) for useful discussions. We acknowledge gratefully the skilled experimental contributions to our program of photoacoustic spectroscopy by Mrs. Lai-Im Lancaster, Mrs. Anita DuPressoir (nee Mac Eachern), and Mr. James Fahey.

REFERENCES

1 A. G. Bell, Am. J. Sci., 20 (1880) 305; Phil. Mag., 11 (1881) 510.

2 A. Rosencwaig and A. Gersho, Science, 190 (1975) 556; J. Appl. Physics, 47 (1976) 64.

3 A. Rosencwaig, Photoacoustics and Photoacoustic Spectroscopy, John Wiley & Sons, Inc., 1980.

4 J. F. McClelland, Analyt. Chem., 55 (1983) 89A.

5 J. C.Donini and K. H.Michaelian,, Infrared Physics, 24 (1984) 157.

6 C. A. Rhoads, J. T. Senftle, M. M. Coleman, A. Davis, and P. C. Painter, Fuel, 62 (1983) 1387.

7 M. C. Lin, F. E. Huggins, G. P. Huffman, and D. E. Lowenhaupt, Prepr. Div. Petroleum Chem. Am. Chem. Soc. 28 (1983) 1196.

8 M. G.Rockley and J. P. Devlin, Appl. Spectroscopy, 34 (1980) 407.

9 J. C.Donini, S. A. LaCour, B. M. Lynch, and A.Simon, in Coal: Phoenix of the '80s: Proc. 1981 Chemical Institute of Canada Coal Symposium. 1982. Volume 1, 132.

10 P. L. Chien, R. Markuszewski, and J. F. McClelland, Prepr. Div. Fuel Chem. Am. Chem. Soc., 30 (1985) 13.

11 T. Zerlia, Appl. Spectroscopy, 40 (1986) 214.

12 N. E.Cooke, O. M. Fuller, and R. P.Gaikwad, Fuel, 65 (1986) 1254.

13 R. Liotta, Fuel 58 (1979) 724.

14 R. Liotta, K. Rose, and E. Hippo, J. Org. Chem. 46 (1981) 277.

15 R. Liotta and G. Brons, J. Am. Chem. Soc. 103 (1981) 1735.

16 B. M. Lynch and A. M. Mac Eachern, Proc. 1983 Conf. Coal Science, pp.653-654.

17 N. R. Smyrl and E. L. Fuller, in E. L. Fuller, Ed. Coal and Coal Products: Analytical Characterization Techniques. ACS Symposium Series 205 (1983) 133.

18 P. R. Griffiths, S. Wang, I. M. Hamadeh, P. W. Yang, and D. E. Henry, Prepr. Div. Fuel Chem. Am. Chem. Soc. 28 (1983) 27.

19 L. F. Fieser and M. Fieser, Reagents for Organic Synthesis John Wiley & Sons, Inc. 1967. p. 1049.

20 M. Kornblum and H. E. de la Mare, J. Am. Chem. Soc. 73 (1951) 880.

21 Y. Sprinzak, J. Am. Chem. Soc. 80 (1958) 5449.

22 B. Plesnicar, in S. Patai, Ed. The Chemistry of Peroxides. John Wiley & Sons, Inc., 1979, p. 573.

23 N. Berkowitz, An Introduction to Coal Technology, Academic Press, 1979. p. 96.

24 D. W. Van Krevelen, Coal. Typology-Chemistry-Physics-Constitution. Elsevier Scientific Publishing Company. 1981, pp.238-262.

25 R. E. Jones and D. T. A. Townend, J. Soc. Chem. Ind. London 68 (1949) 197.

26 C. A. Yohe and C. A. Harman, J. Am. Chem. Soc. 64 (1942) 1809.

27 H. A. W. de Vries, C. Bokhoven, and H. H. Dormans, Brennst. Chem. 50 (1959) 289.

28 S. L. Chakravarty, J. Mines, Metals, Fuels (1960) pp.1, 10.

29 B. M. Lynch, Proc. Soc. Photo-Optical Instr. Engineers 553 (1985) 320.

30 B. M. Lynch, L. Lancaster, and J. T. Fahey, Prepr. Div. Fuel Chem. Am. Chem.Soc. 31 (1986) 43.

31 J. S. Gethner, Prepr. Div. Fuel Chem. Am. Chem. Soc. 31 (1986) 103.

32 M. Guiliano, J. Kister, and H. Dou, Compt. rend. Acad. Sci Paris 302 (1986) 621.

33 R. J. Mikula, D. E. Axelson, and K. H. Michaelian, Proc. 1985 Conference on Coal Science, 495.

34 P. L. Chien, R. Markuszewski, and J. F. McClelland, Proc. 1985 Conf. Coal Science, 818.

35 P. B. Tooke and A. Grint, Fuel 62 (1983) 1003.

36 P. C. Painter, M. M. Coleman, R. W. Snyder, O. Mahajan, M. Kamatsu, and P. L. Walker, Appl. Spectroscopy 35 (1981) 106.

37 B. S. Ignasiak, A. J. Szladow, and D. S. Montgomery, Fuel 53 (1974) 12.

38 L. M. Stock and S. H. Wang, Prepr. Div. Fuel Chem. Am. Chem.Soc. 31 (1986) 49.

39 P. M. Fredericks, P. R. Osborn, and D. A. J. Swinkels, Fuel 63 (1984) 139.

40 J. W. Larsen and T. E. Schmidt, Fuel 65 (1986) 131.

2.

CARBONYL GROUPS FROM CHEMICALLY AND THERMALLY PROMOTED DECOMPOSITION OF PEROXIDES ON COAL SURFACES: DETECTION OF SPECIFIC TYPES OF USING PHOTOACOUSTIC INFRARED FOURIER TRANSFORM SPECTROSCOPY,

by

Brian M. Lynch, Lai-Im Lancaster, and J. Anthony MacPhee.

Fuel, Volume 66, to be published in the July 1987 issue.

Carbonyl groups from chemically and thermally promoted decomposition of peroxides on coal surfaces

Detection of specific types using photoacoustic infrared Fourier transform spectroscopy*

Brian M. Lynch, Lai-Im Lancaster and J. Anthony MacPhee

*Preprinted from Fuel, Volume 66, July 1987 issue (a special issue on "New Applications of Analytical Techniques to Fossil Fuels")

Carbonyl groups from chemically and thermally promoted decomposition of peroxides on coal surfaces

Detection of specific types using photoacoustic infrared Fourier transform spectroscopy*

Brian M. Lynch, Lai-Im Lancaster and J. Anthony MacPhee†
Department of Chemistry, St Francis Xavier University, Antigonish, Nova Scotia B2G 1C0, Canada
†Energy Research Laboratories, CANMET Energy, Mines, and Resources Canada, Ottawa, Ontario K1A 0G1, Canada
(Received 3 November 1986; revised 22 January 1987)

Detection of new carbonyl-type functionality at the surfaces of powdered bituminous coals is illustrated by the technique of photoacoustic infrared Fourier transform (PAIFT) spectroscopy. These species are generated both by base-promoted and by thermal decompositions of precursor peroxides, postulated as ubiquitous constituents at the surfaces of all except the most freshly prepared samples. In artificially oxidized coals, there are quantitative associations between the level of thermally generated carbonyl content revealed by PAIFT spectra and plastic properties of the coals.

(Keywords: coal surfaces; photoacoustic FT-i.r.; carbonyl group; peroxides)

Over the past three years, the authors have generated a data base of photoacoustic infrared Fourier transform (PAIFT) spectra of coal samples amounting to several thousand spectra. Various preliminary reports of these findings have been published or presented[1-7].

Among the manifold advantages possessed by PAIFT spectroscopy for the study of coals are minimal sample preparation, insensitivity of signal to degree of subdivision, and the ability to observe surface features generated by chemical transformations. PAIFT spectra of coals do not exhibit the sloping baselines characteristic of alkali halide pellet spectra (contrast a recent report of such FT-i.r. spectra of Canadian coals[8]), and direct subtraction to yield difference spectra revealing introduced features is straightforward and avoids arbitrary scaling procedures.

This paper reports detection by PAIFT spectroscopy of new carbonyl oxygen functions at the surfaces of powdered bituminous coals, which derive from base-promoted or thermal decompositions of precursor peroxide species, which are suggested to be present ubiquitously as surface entities for all except the most freshly prepared samples. The thermal decompositions accompany a standard vacuum drying procedure and have probably escaped previous detection since the grinding procedures associated with sample preparation for K Br-pellet transmission FT-i.r. and diffuse reflectance FT-i.r. spectroscopic measurements impose randomization and dilution of surface infrared absorbing groups.

* This paper was presented at the American Chemical Society Symposium 'New Applications of Analytical Techniques to Fossil Fuels', held at New York City, USA, May 1986

EXPERIMENTAL

PAIFT spectra

Spectra were obtained using a Bruker IFS110 purge-type infrared Fourier system with a germanium on potassium bromide beamsplitter. The interferometer compartment of the spectrometer was acoustically insulated from the sample compartment using a box fabricated from expanded polystyrene. The modulated source radiation was reflected into an EG & G Princeton Applied Research Model 6003 Photoacoustic accessory fitted with a zinc selenide window, and the amplified photoacoustic output was transmitted to the data system of the IFS110. The nitrogen purge flow was interrupted during scanning.

In the standard operating mode, the dried coal (10–50 mg) was placed in the sample cup, and 128 photoacoustic interferograms were collected at 8 cm^{-1} resolution with a zero-filling factor of 2, corresponding to a final transformed spectrum encoded every 4 cm^{-1}. The photoacoustic spectra were obtained by ratioing against the energy output (black-body response) from a similarly dried sample of Fisher Carbon Lampblack C-198. The interferometer mirror velocity was 0.08333 cm s^{-1}, and spectra were acquired from 4000 to 400 cm^{-1}. Difference spectra were obtained by least-squares subtraction, i.e. difference intensity = (spectrum of treated coal) − x(spectrum of untreated coal), where x = the subtraction coefficient. Subtractions were effected on the digitized spectra under the control of the ATS85 instrument software package on a Bruker Aspect 2000 computer. Sets of individual spectra of different portions of the coal samples (generally four to six per set) gave matching

Table 1 Coal samples subjected to high-pressure oxidations: analytical and fluidity data on fresh coals

Coal designation	Classification	Analysis (wt%, daf) C	H	O	Gieseler fluidity (dd/min)*
C-1 (Western Canadian)	HV'A'	80.5	5.1	5.6	365
C-2 (Western Canadian)	HV'A'	81.6	4.8	4.8	24
A-1 (Appalachian, USA)	HV'A'	79.7	5.2	7.5	1580
A-2 (USA)	HV'A'	81.8	5.1	4.3	20350
A-3 (USA)	MV–HV'A'	83.1	4.7	3.8	7900
A-4 (USA)	L–MV	85.0	4.4	3.2	32

* dd/min = dial divisions per minute

spectra [i.e. zero baseline over the ranges used for subtractions (2000–1400 cm^{-1} for the chemically treated samples or 2000–1500 cm^{-1} for samples subjected to high-pressure oxidations)]. The subtraction coefficients x were in the range 0.99–1.01.

Preparation of coal samples for spectroscopy

The Cape Breton coals were ground to the range 50–60 mesh under liquid nitrogen using a Brinkmann Pulverizer, and were dried at 100°C under vacuum for 6 h before transfer to the sample cup of the photoacoustic accessory.

Coal samples subjected to high-pressure oxidations

The coals were ground and sized to 50 mesh and were subjected to oxidation by air at 55°C and 9 MPa for periods ranging from 3 to 196 h. All samples were subjected to the standard drying procedure before PAIFT spectroscopic examination.

Analytical and fluidity data on these as-received coal samples are presented in *Table 1*.

RESULTS AND DISCUSSION

Carbonyl functionalities from base-promoted decomposition reactions

The recorded sensitivity of FT-i.r. spectroscopy in detecting oxidative change in coals is significantly less than that of standard plasticity tests; thus, Painter and co-workers[9], employing standard KBr-pellet 'transmission' FT-i.r. spectroscopy, found < 1% increase in the ratioed intensity of carbonyl bands for coals oxidized at 60°C or 140°C for periods sufficient to decrease Gieseler fluidity by over 90%.

As part of a programme of exploration of the scope of PAIFT spectroscopy in coal characterization, the present authors have explored the quantitative methylation of bituminous coals using phase-transfer catalysed processes which are based upon those developed by Liotta and co-workers[10–12]. These procedures involve initial formation of anionic centres by deprotonation of acidic oxygen functions, effected by treatment with tetra-*n*-butylammonium hydroxide in aqueous tetrahydrofuran under nitrogen, followed by S_N2 reaction with iodomethane, as in:

$$\text{coal}.OH + NBu_4^+ + OH^- \rightarrow \text{coal}.O^- + NBu_4^+ + H_2O$$

$$\text{coal}.O^- + CH_3.I \rightarrow \text{coal}.OCH_3 + I^-$$

Figure 1 reproduces PAIFT spectra for a typical sample of freshly ground, newly mined bituminous coal from Cape Breton Island, Nova Scotia (*Figure 1a*), and of its product of quantitative methylation (*Figure 1b*). Noteworthy features in the spectrum of the methylation product are the horizontal baseline patterns and the absence of O–H absorptions. In previously reported work[1–4] it was remarked that PAIFT spectra of methylated samples of many bituminous coals also exhibit distinct carbonyl absorption in the 1680–1705 cm^{-1} region not shown by the original coal.

Although such results may, possibly, be explained by a high-frequency shift of a pre-existing carbonyl species caused by removal of inter-group hydrogen-bonding interactions, supplementary experiments show that the new carbonyl species arise irreversibly at the stage of coal anion formation, *before* the methylation step. The overlay spectrum of *Figure 2* illustrates this point. The new peak is unchanged after re-acidification of the reaction mixture and thus cannot involve displacement of a carboxylate: carboxylic acid ratio.

The overlay spectrum (*Figure 2*) for the coal of *Figure 1*

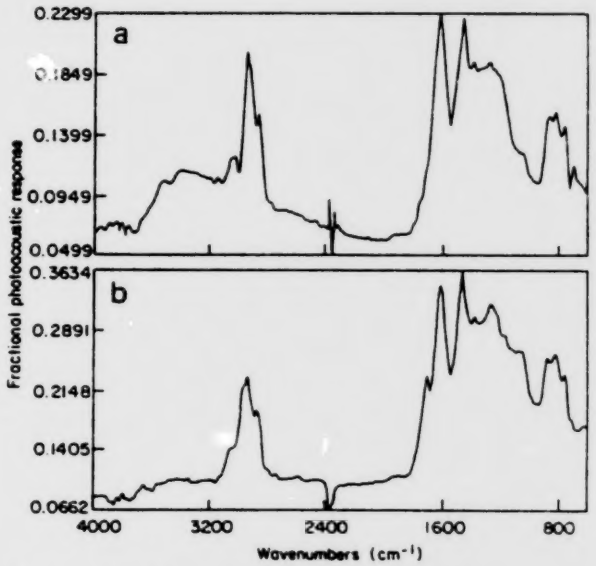


Figure 1 Typical PAIFT spectra of (a) Cape Breton Island bituminous coal no. P-303 and (b) its product of phase-transfer methylation

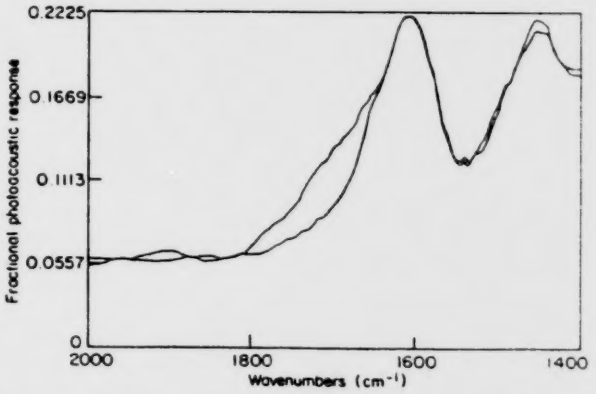


Figure 2 Overlay PAIFT spectra (2000–1400 cm^{-1}) of the coal of *Figure 1* before and after coal anion generation

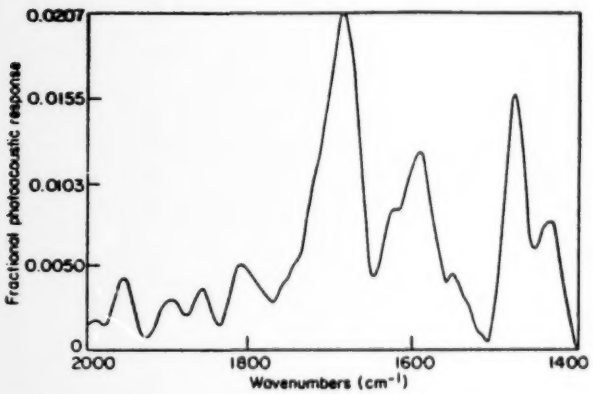


Figure 3 Difference spectrum corresponding to *Figure 2*

and the corresponding reprotonated 'coal anion' (re-acidified and thoroughly washed) indicates asymmetry between 1600–1700 cm^{-1}, and the digitized difference spectrum for these samples (*Figure 3*) reveals a simple carbonyl peak with maximum at 1686 cm^{-1}, classified here as an aralkyl ketone. Chemical confirmation of assignment as a ketone is provided by reduction of the base-treated coal by tetrabutylammonium borohydride in aqueous tetrahydrofuran, eliminating the carbonyl absorption peak. Acetylation of the reduction product (involving heating under reflux with an acetic anhydride–pyridine mixture) leads to a product with identifiable alcoholic acetate absorption at 1736 cm^{-1}, in addition to the principal phenolic acetate features around 1760–1765 cm^{-1}. The reactions effected are:

$$\text{coal}.C(O)R \xrightarrow{NBu_4^+ BH_4^-,\ THF/H_2O} \text{coal}.CH(OH)R$$

$$\text{coal}.CH(OH)R \xrightarrow{(CH_3CO)_2O,C_5H_5N} \text{coal}.CH(OC(O)CH_3)R$$

It is well documented (see, e.g., Ref. 13) that borohydride ion reductions are specific for ketone → alcohol conversions, without affecting carboxylic acid functions.

The formation of these new absorbing entities is attributed here to the base-promoted decompositions of peroxide species, i.e.

$$\text{coal}.CH(R)OOR' + OH^- \rightarrow \text{coal}.C(O)R + R'O^- + H_2O$$

(R = alkyl or aralkyl; R' = H, alkyl or aralkyl)

Such reactions for simple organic peroxides are well documented[14–16], but their possible relevance to coal transformations has not been recognized previously. Although it is generally accepted[17,18] that peroxy species are generated in the initial stages of oxidation of bituminous coals at moderate temperatures, the major supporting evidence derives from the non-spectroscopic studies by Jones and Townend[19], Yohe and Harman[20], deVries and co-workers[21] and Chakravarty[22]. The results presented here are the first spectroscopic evidence supporting the postulated intermediacy of peroxides for coals oxidized by simple aerial exposure at routine laboratory temperatures. As far as the authors are aware, all previous FT-i.r. studies of coal oxidations where development of carbonyl absorptions has been detected refer to oxidations at 100°C or above (for examples, see Refs. 9, 23–31).

If the original coal sample of *Figure 1* is derivatized through quantitative acetylation, added ketone-type carbonyl absorptions derived from the coal itself are not detectable. Under these conditions, it is likely that the superficial peroxides transfer oxygen to the pyridine solvent yielding pyridine 1-oxide, without generating carbonyl species.

It should be noted that although the overlay and the difference spectra illustrated in *Figures 2* and *3* bear a general resemblance to patterns for the same coal oxidized intentionally at higher temperature (see *Figures 4* and *5*), the band shapes in the carbonyl region are distinctly different; the carbonyl-region absorption in *Figure 5* obviously possesses multiple contributing features.

The intensities of the ketone carbonyl peaks in the difference spectra derived from base-treatment of the same coal after storage in the laboratory at ≈ 20°C for six and for twelve months increase progressively: 'freshly prepared' coal (as illustrated in *Figure 3*), 0.020 intensity units; after six months, 0.059; after twelve months, 0.089.

The restoration of the large dilatation of slightly oxidized high-volatile bituminous coals by treatment with aqueous barium hydroxide, noted previously by Ignasiak, Szladow and Montgomery[32], is readily explained by occurrence of base-promoted decompositions of peroxide species generated at the coal surfaces.

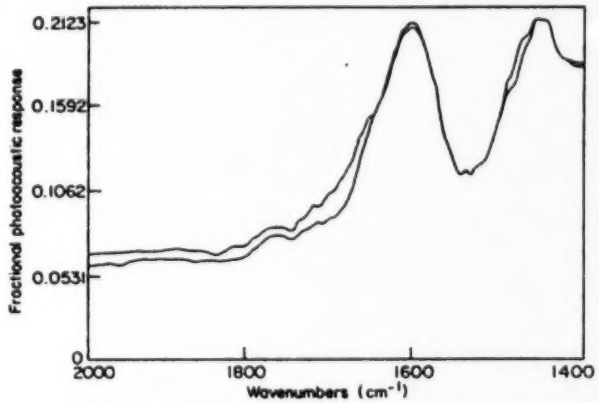


Figure 4 Overlay PAIFT spectra (2000–1400 cm^{-1}) of the coal of *Figure 1* revealing changes after thermal oxidation in air at 105°C for 24 h

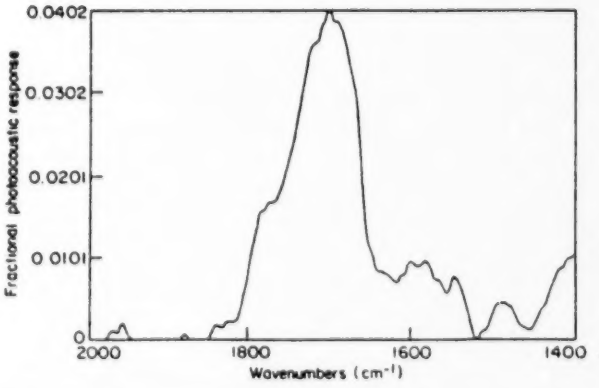


Figure 5 Difference spectrum corresponding to *Figure 4*

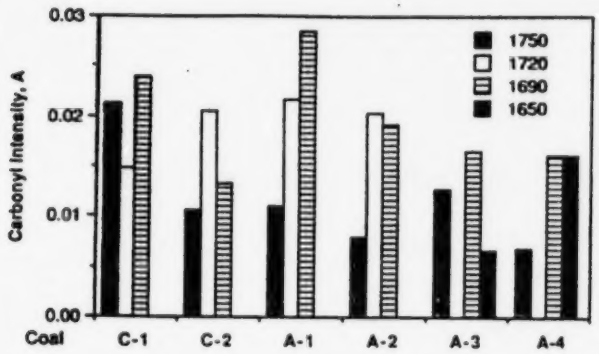


Figure 6 Data from difference spectra (oxidized 48 h – fresh coal, 2000–1500 cm^{-1}) for six coals of *Table 1* oxidized at high pressure, illustrating distinctive carbonyl-peak patterns

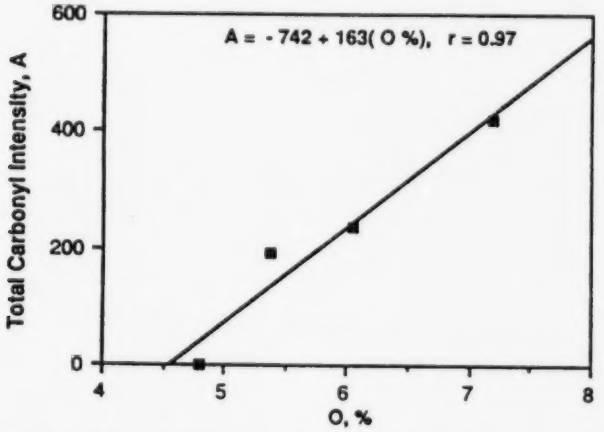


Figure 7 Carbonyl intensity (from PAIFT spectra) *versus* oxygen content for bituminous coal C-2

Carbonyl functionalities from coals subjected to 'accelerated oxidations' at high pressure

In work supplemental to that reported previously[6,7], it has been possible to compress the time scale of the oxidative changes using a series of experiments where the powdered coals were subjected to pressurized air at slightly elevated temperatures. With these samples, it was found that the standard vacuum drying procedure had effected thermal decompositions of the assumed peroxide species, generating distinct, readily differentiated types of carbonyl absorptions whose relative proportions are different for the different coals.

The classes of carbonyl absorptions appearing are around 1750, 1720, 1690 and 1650 cm^{-1}, and the distributions of carbonyl peak intensities (derived from difference spectra) are reproduced in bar-graphical form in *Figure 6* for the six coals of *Table 1* at the stage of 48 h oxidation. Standard interpretations based on characteristic infrared frequency tables (e.g. Bellamy[33]) suggest that these peaks arise from different, specific decompositions of peroxides occupying different structural sites in the coals. The 1750 cm^{-1} and 1720 cm^{-1} peaks are attributed to decompositions of α-hydroperoxyethers to yield cyclic or open-chain esters, the 1750 cm^{-1} (lactone species) from a cyclic ether precursor, and the 1720 cm^{-1} from an open-chain precursor, i.e.

$$ArOCH_2R \xrightarrow{O_2,\ 55°C,\ 9\ MPa} ArOCH(OOH)R$$

$$ArOCH(OOH)R \xrightarrow{100\ C,\ vacuum} ArOC(O)R$$

Stock and Wang[34] have recently postulated generation of lactone species from the ruthenium(VIII)-catalysed oxidation of Illinois no. 6 bituminous coal by sodium periodate.

The 1690 and 1650 cm^{-1} peaks are attributed to decompositions of α-hydroperoxy aralkanes or of hydroperoxy diarylalkanes, i.e.

$$ArCH_2R \xrightarrow{O_2,\ 55\ C,\ 9\ MPa} ArCH(OOH)R$$

$$ArCH(OOH)R \xrightarrow[(R = alkyl\ or\ aryl)]{100\ C,\ vacuum} ArC(O)R$$

Associations of carbonyl absorption intensities with other coal properties

The relative proportions of the four carbonyl absorptions for the six coals examined are dependent in a complex manner upon oxygen content, carbon/hydrogen ratio and the progress of oxidation, but there are *quantitative* associations of increasing carbonyl intensities with many characteristics of the behaviour of the sequences of oxidized samples for a given coal. As examples, linear relationships link total thermally generated carbonyl intensity and (directly determined) oxygen content for the bituminous high-volatile 'A' coals C-2 (Western Canadian) and A-1 (Appalachian) (*Figures 7* and *8*), and a generalized relationship relates carbonyl intensities to the logarithims of the normalized Gieseler fluidity (for all six coals, 26 data pairs) (*Figure 9*). However, the coals behave in sufficiently different fashions (in the quantitative distribution of the various introduced carbonyl species, in their qualitative rates of generation, and in the details of the influence of changed functionality on the technical properties) that generalized treatment as a single data set tends to obscure the individual correlations.

Thus for the individual sets of coal samples, the separate relationships between the logarithms of Gieseler

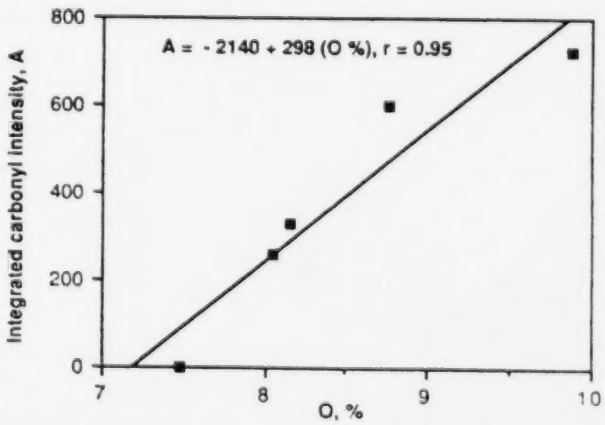


Figure 8 Carbonyl intensity (from PAIFT spectra) *versus* oxygen content for bituminous coal A-1

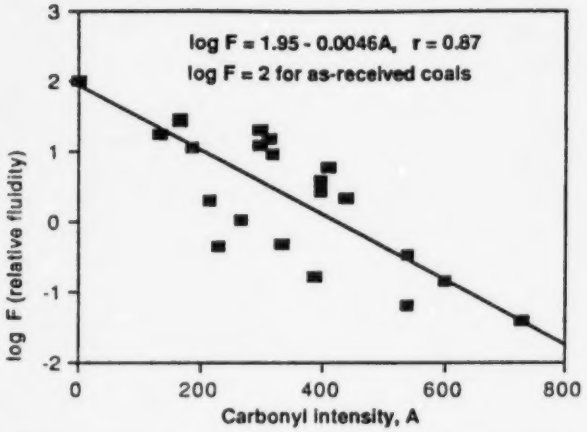


Figure 9 Normalized fluidity (log scale) *versus* carbonyl intensity (from PAIFT spectra) for six coals at various oxidation stages (26 data pairs)

Table 2 Linear correlations between logarithm of Gieseler fluidity and carbonyl intensity, $\log F = a(\text{CO intensity}) + \log F_0$

Coal designation	a	$\log F_0$, calc.*	Correlation coefficient (r^2)
C-1	0.0078	2.62 (2.56)	0.940
C-2	0.0079	1.27 (1.38)	0.980
A-1	0.0043	2.75 (3.20)	0.950
A-2	0.0056	4.64 (4.31)	0.950
A-3	0.0071	4.19 (3.89)	0.950
A-4	0.0034	1.56 (1.51)	0.970

*Observed values in parentheses

fluidity and carbonyl intensity are of significantly higher quality than for the merged set (see *Table 2*). In view of such findings, it is suggested that caution would be appropriate in using the approaches adopted by Fredericks and co-workers[35], where attempts are made to make generalized predictions of technological properties using principal factor analyses of FT-i.r. spectra of a wide range of coals.

CONCLUSIONS

The evidence for previously unquantified and undetected peroxide species on coal surfaces requires reconsideration of the influence of the proportion of surface peroxides upon the course(s) of coal pyrolyses, and supports recent proposals[36] recommending storage of laboratory samples of coals in sealed ampoules. These recommendations have been adopted for the Premium Coal Sample programme administered by the Argonne National Laboratory.

ACKNOWLEDGEMENTS

The authors thank Drs J. S. Gethner and R. Liotta (Exxon Research and Engineering Company) and Dr R. A. Durie (R. W. Miller Holdings, Sydney, Australia) for useful discussions. The research work upon which this paper is based was supported by Energy, Mines, and Resources Canada through the Department of Supply and Services, contract serial nos. OST83-00347 and OST85-00235, and under research agreements nos. 230 (1985–1986) and 189 (1986–1987).

REFERENCES

1 Campbell, M., Lancaster, L., Lynch, B. M. and MacEachern, A. M. Conf. Anal. Chem. Appl. Spectrosc., Pittsburgh, 1983, Abstract 054
2 Lancaster, L., Lynch, B. M., MacEachern, A. M., Donini, J. C., Hamza, H. and Michaelian, K. H., 57th Colloid and Surface Sci. Symp., Am. Chem. Soc., 1983, Abstract 158
3 Lynch, B. M. and MacEachern, A. M., Proc. 1983 Conf. Coal Sci., 653
4 Lynch, B. M., Lancaster, L., MacEachern, A. M. and Khan, M. A., Eastern Anal. Symp., Am. Chem. Soc., 1983, Paper 161
5 Lynch, B. M. *Bull. Am. Phys. Soc.* 1985, **30**, 504
6 Lynch, B. M. *Proc. Soc. Photo-Optical Instr. Engineers* 1985, **553**, 320
7 Lynch, B. M., Lancaster, L. and Fahey, J. T. *Am. Chem. Soc. Div. Fuel Chem., Prepr.* 1986, **31**, 43
8 Cooke, N. E., Fuller, O. M. and Gaikwad, R. P. *Fuel* 1986, **65**, 1254
9 Rhoads, C. A., Senftle, J. T., Coleman, M. M., Davis, A. and Painter, P. C. *Fuel* 1983, **62**, 1387
10 Liotta, R. *Fuel* 1979, **58**, 724
11 Liotta, R., Rose, K. and Hippo, E. *J. Org. Chem.* 1981, **46**, 277
12 Liotta, R. and Brons, G. *J. Am. Chem. Soc.* 1981, **103**, 1735
13 Fieser, L. F. and Fieser, M. 'Reagents for Organic Synthesis', John Wiley & Sons, New York, 1967, p. 1049
14 Kornblum, M. and De la Mare, H. E. *J. Am. Chem. Soc.* 1951, **73**, 880
15 Sprinzak, Y. *J. Am. Chem. Soc.* 1958, **80**, 5449
16 Plesnicar, B. in 'The Chemistry of Peroxides' (Ed. S. Patai), John Wiley & Sons, New York, 1979, p. 573
17 Berkowitz, N. 'An Introduction to Coal Technology', Academic Press, New York, 1979, p. 96
18 Van Krevelen, D. W. 'Coal. Typology-Chemistry-Physics-Constitution', Elsevier, Amsterdam, 1981, pp. 238–262
19 Jones, R. E. and Townend, D. A. T. *J. Soc. Chem. Ind. London* 1949, **68**, 197
20 Yohe, G. R. and Harman, C. A. *J. Am. Chem. Soc.* 1942, **64**, 1809
21 deVries, H. A. W., Bokhoven, C. and Dormans, H. H. *Brennst. Chem.* 1959, **50**, 289
22 Chakravarty, S. L. *J. Mines, Metals, Fuels* 1960, 1 and 10
23 Gethner, J. S. *Am. Chem. Soc. Div. Fuel Chem., Prepr.* 1986, **31**, 103
24 Zerlia, T. *Appl. Spectrosc.* 1986, **40**, 214
25 Guiliano, M., Kister, J., Mille, G. and Dou, H. *Compt. Rendu. Acad. Sci. Paris* 1986, **302**, 621
26 Mikula, R. J., Axelson, D. E. and Michaelian, K. H. Proc. 1985 Conf. Coal Sci. 495
27 Chien, P. L., Markuszewski, R. and McClelland, J. F. *Am. Chem. Soc. Div. Fuel Chem., Prepr.* 1985, **30**, 13
28 Chien, P. L., Markuszewski, R. and McClelland, J. F. Proc. 1985 Conf. Coal Sci. 818
29 Tooke, P. B. and Grint, A. *Fuel* 1983, **62**, 1003
30 Smyri, N. R. and Fuller, E. L. in 'Coal and Coal Products: Analytical Characterization Techniques' (Ed. E. L. Fuller), Am. Chem. Soc. Symp. Ser. 1982, **205**, 133
31 Painter, P. C., Coleman, M. M., Snyder, R. W., Mahajan, O., Komatsu, M. and Walker, P. L. *Appl. Spectrosc.* 1981, **35**, 106
32 Ignasiak, B. S., Szladow, A. J. and Montgomery, D. S. *Fuel* 1974, **53**, 12
33 Bellamy, L. J. 'The Infra-red Spectra of Complex Molecules', 3rd Ed., Chapman and Hall, London, 1978, p. 7
34 Stock, L. M. and Wang, S. H. *Am. Chem. Soc. Div. Fuel Chem., Prepr.* 1986, **31**, 49
35 Fredericks, P. M., Osborn, P. R. and Swinkels, D. A. J. *Fuel* 1984, **63**, 139
36 Larsen, J. W. and Schmidt, T. E. *Fuel* 1986, **65**, 1310

3.

CHARACTERIZATION OF SURFACE FUNCTIONALITY OF COALS BY PHOTOACOUSTIC FTIR (PAIFT) SPECTROSCOPY, REFLECTANCE INFRARED MICROSPECTROMETRY, AND X-RAY PHOTOELECTRON SPECTROSCOPY.

By
Brian M. Lynch, Lai-Im Lancaster,
and J. Anthony MacPhee.

Symposium: Surface Chemistry of Coals.-
Preprints, Division of Fuel Chemistry, American Chemical Society,
Volume 32, No. 1, 138-145 (1987).
To be published in full in Energy and Fuels,
Volume 2, issue 1 (1988).

CHARACTERIZATION OF SURFACE FUNCTIONALITY OF COALS BY PHOTOACOUSTIC FTIR (PAIFT) SPECTROSCOPY, REFLECTANCE INFRARED MICROSPECTROMETRY, AND X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

Brian M. Lynch, Lai-Im Lancaster,
and J. Anthony MacPhee*

Department of Chemistry, St. Francis Xavier University,
Antigonish, Nova Scotia B2G 1C0, Canada

This paper illustrates detection by the technique of PhotoAcoustic Infrared Fourier Transform (PAIFT) spectroscopy of new carbonyl-type functionality at the surfaces of powdered bituminous coals, generated by both base-promoted and by thermal decomposition of precursor peroxide species, postulated as ubiquitous constituents at the surfaces of all except the most freshly prepared samples. In artificially oxidized coals, there are quantitative associations between the level of carbonyl content revealed by PAIFT spectra and plastic properties of the coals. In additional, related studies, we have derivatized and quantified the hydroxyl group content of the oxidized coals by trifluoroacetylation, followed by hydrolysis and anion-chromatographic analyses for trifluoroacetate. PAIFT and Fluorine-XPS spectra of the trifluoroacetylated species are discussed. Maceral components and mineral inclusions have been identified and characterized in sectioned, polished surfaces of Canadian bituminous coals using reflection FTIR microspectrometry; this direct examination shows promise for real-time monitoring of various reactions at surfaces.

INTRODUCTION

Sensitivity enhancements in spectroscopy show promise of specific characterization of functional groups in coals and their chemical transformations. We have applied one of the newer techniques (PhotoAcoustic Infrared Fourier Transform spectroscopy (PAIFT spectroscopy)) to generate a data base of coal samples amounting to several thousand spectra. Various preliminary reports of our results have been published or presented (1-7).

Among the manifold advantages possessed by PAIFT spectroscopy for the study of coals are minimal sample preparation, insensitivity of signal to degree of subdivision, and the ability to observe surface features generated by chemical transformations. PAIFT spectra of coals do not exhibit the sloping baselines characteristic of alkali halide pellet spectra (contrast a recent report of such FTIR spectra of Canadian coals (8)), and subtraction to yield difference spectra revealing introduced features is straightforward and avoids arbitrary scaling procedures. The first paper of this series (7) reported detection by PAIFT spectroscopy of new carbonyl oxygen functions at the surfaces of powdered bituminous coals, derived from base-promoted or thermal decompositions of precursor peroxide species, which we suggested were present ubiquitously as surface entities for all except the most freshly prepared samples. In more recent work, we have discovered that thermal decompositions accompany a standard vacuum drying procedure.

---

*Energy Research Laboratories, CANMET, Energy, Mines and Resources Canada, Ottawa, Canada K1A 0G1

EXPERIMENTAL

PhotoAcoustic Infrared Fourier Transform (PAIFT) Spectra

Spectra were obtained using a Bruker IFS110 purge-type Infrared Fourier System with a Ge on KBr beamsplitter. The interferometer compartment of the spectrometer was acoustically insulated from the sample compartment using a box fabricated from expanded polystyrene. The modulated source radiation was reflected into a E G & G Princeton Applied Research Model 6003 Photoacoustic accessory fitted with a zinc selenide window and the amplified photoacoustic output was transmitted to the data system of the IFS110. The nitrogen purge flow was interrupted during scanning.

In the standard operating mode, 10-50 mg of the dried coal were placed in the sample cup, and 128 photoacoustic interferograms were collected at 8 $cm.^{-1}$ resolution with a zero-filling factor of 2, corresponding to a final transformed spectrum encoded every 4 $cm.^{-1}$. The photoacoustic spectra were obtained by ratioing against the energy output (black-body response) from a similarly dried sample of Fisher Carbon Lampblack C-198. The interferometer mirror velocity was 0.08333 cm s^{-1}, and spectra were acquired from 4000 to 400 $cm.^{-1}$. The difference spectra illustrated in Figures 1 through 6 were obtained by least-squares subtraction over the range 2000-1400 $cm.^{-1}$.

Preparation of Coal Samples for Spectroscopy

The coals were ground to the range 50-60 mesh under liquid nitrogen using a Brinkmann Pulverizer, and were dried at 100°C under vacuum for 6 h before transfer to the sample cup of the photoacoustic accessory.

High-Pressure Oxidations of Coal Samples

The coals were ground and sized to 50 mesh and were subjected to oxidation by air at 55°C and 9 MPa for periods ranging from 3 to 196 h. All samples were subjected to the standard drying procedure before PAIFT spectroscopic examination.

Analytical and fluidity data on the as-received coal samples are presented in Table 1.

FTIR Microspectrometry

Spectra were acquired (250-500 scans) using a Spectra-Tech IR-PLAN accessory and a Nicolet 20SX spectrometer, at a resolution of 4 $cm.^{-1}$; spectra are referenced against an equivalent area of a gold-surfaced mirror.

DISCUSSION AND RESULTS

(a) *Generation of Carbonyl Functionalities from Thermal Decompositions of Peroxides at Surfaces of Coals Subjected to "Accelerated Oxidations" at High Pressure*

The recorded sensitivity of FTIR spectroscopy in detecting oxidative change in coals is significantly less than that of standard plasticity tests; thus, Painter and his colleagues (9), employing standard KBr pellet "transmission" FTIR spectroscopy, found less than a 1 % increase in the ratioed intensity of carbonyl bands for coals oxidized at 60°C or 140°C for periods sufficient to decrease Gieseler fluidity by over 90 %.

We have compressed the time scale of oxidative changes by subjecting powdered coals to pressurized air at slightly elevated temperatures. With such samples, we observe distinct, readily differentiated types of carbonyl absorptions (around 1750, 1720, 1690, and 1650 $cm.^{-1}$) whose relative proportions are *different* for different coals, and we propose that the carbonyl species are generated by the standard vacuum drying procedure from thermal decomposition of the assumed peroxide species. Representative difference spectra taken for the six coals of Table 1 at the stage of 48 hours oxidation are reproduced in Figures 1 through 6.

We suggest that these peaks arise from different, specific decompositions of peroxides occupying different structural sites in the coals. The 1750 $cm.^{-1}$ and 1720 $cm.^{-1}$ peaks are attributed to decompositions of α–hydroperoxyethers to yield cyclic or open-chain esters; the 1750 $cm.^{-1}$ (lactone species) from a cyclic ether precursor, and the 1720 $cm.^{-1}$ from an open-chain precursor, that is:

$$Ar.O.CH_2.R \xrightarrow{(O_2,\ 55^{\circ}C,\ 9\ MPa)} Ar.O.CH(O.O.H).R$$

$$Ar.O.CH(O.O.H).R \xrightarrow{(100^{\circ}C,\ vacuum)} Ar.O.CO.R$$

Stock and Wang (10) have recently postulated generation of lactone species from the ruthenium (VIII)-catalyzed oxidation of Illinois No. 6 bituminous coal by sodium periodate.
The 1690 and 1650 $cm.^{-1}$ peaks are attributed to decompositions of α–hydroperoxy aralkanes or of hydroperoxy diarylalkanes, that is:

$$Ar.CH2.R \xrightarrow{(O_2,\ 55^oC,\ 9\ MPa)} Ar.CH(O.OH)R$$

$$Ar.CH(O.OH)R \xrightarrow{(100^oC,\ vacuum)} Ar.CO.R$$

$$Ar.CH_2.Ar \xrightarrow{(O_2,\ 55^oC,\ 9\ MPa)} Ar.CH(O.OH)Ar$$

$$Ar.CH(O.OH)Ar \xrightarrow{(100^oC,\ vacuum)} Ar.CO.Ar$$

(b) *Associations of Carbonyl Absorption Intensities with Other Coal Properties*

The relative intensities of the four carbonyl absorptions for the six coals examined are dependent in a complex manner upon oxygen content, carbon/hydrogen ratio, and the progress of oxidation, but there are general *quantitative* associations of increasing carbonyl intensities with many characteristics of the behavior of the sequences of oxidized samples for a given coal. These include relationships between carbonyl intensity and oxygen content for the Greenhills coal (Western Canadian: bituminous high-volatile 'A'), carbonyl intensity and Gieseler fluidity for the Greenhills and Fording (Western Canadian: bituminous high-volatile 'A') coals, and for the Barton and McClure coals (U.S.A., bituminous high-volatile 'A' and medium-high volatile 'A'), illustrated in Figures7 through 13. However, the coals are behaving in sufficiently different fashions (both in the quantitative distribution of the various introduced carbonyl species, in the their qualitative rates of generation, and in the nature of the influence of changed functionality on the technical properties) that generalized treatment as a single data set would obscure the individual correlations. In view of our findings, we suggest that caution would be appropriate in using the approaches adopted by Fredericks and his co-workers (11), where attempts are made to make generalized predictions of technological properties using principal factor analyses of FTIR spectra of a wide range of coals.

(d) *Trifluoroacetylation as a Derivatization Technique for Hydroxyl Content of Coals*

Acetylation via acetic anhydride/pyridine is a standard derivatization method for analysis of hydroxyl content of coals, but the quantitative nature and the selectivity of these reactions are not established; there are significant difficulties in using FTIR difference spectroscopy and the acetate carbonyl intensity to define the nature of hydroxyl groups (that is, phenolic or alcoholic?). Since these differences arise in part from peak overlap of acetate carbonyl with the 1600 $cm.^{-1}$ absorption of coals, we have employed trifluoroacetylation (where the trifluoroacetate carbonyl absorbs around 1800 $cm.^{-1}$) as an alternate technique. The trifluoroacetate ion may be analyzed readily by anion chromatography after hydrolysis of the trifluoroacetylated coal, and quantitation of the trifluoroacetyl group is also possible by calibration against the intensity of the fluorine and trifluoromethyl-carbon signals in the X-ray photoelectron spectra of such samples.

(e) *Reflection FTIR Microspectrometry of Coals*

We have conducted preliminary examinations of sectioned, polished surfaces of samples of Eastern and Western Canadian bituminous coals using the IR-PLAN accessory in the reflectance mode, referenced against a gold mirror. Representative spectra are reproduced as Figures 14 through 17. The significant differences among the microscopically distinguishable components, and the ease of detection and identification of mineral inclusions, suggest that direct examinations of coals undergoing chemical transformations (such as the base-promoted and thermal transformations discussed in this paper and our earlier work) could be profitably examined using this accessory FTIR device.

CONCLUSIONS

We have indicated the potential for surface characterization of several techniques under study in our laboratory. We suggest that the evidence for previously unquantified and undetected peroxide species on coal surfaces presented above and in an earlier Symposium (7) requires reconsideration of the influence of the proportion of surface peroxides upon the course(s) of coal pyrolyses, and provides strong support to recent proposals (12) recommending storage of laboratory samples of coals in sealed ampoules.

ACKNOWLEDGEMENTS

We thank Bob Durie, Jon Gethner, and Ron Liotta for useful discussions. The reflection FTIR microspectrometric measurements were made at the Applications Laboratory, Spectra-Tech, Inc., Stamford, Connecticut, and we thank Joan Kwiatkowski and Cindy Friedman for their courtesy. The research work upon which this paper is based was supported by Energy, Mines, and Resources Canada through the Department of Supply and Services, Contract Serial Numbers OST83-00347 and OST85-00235, and under Research Agreements Nos. 230 (1985-1986) and 189 (1986-1987).

REFERENCES

1 Campbell, M., Lancaster, L., Lynch, B. M., and Mac Eachern, A. M. *Abstract 054, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy*, 1983 (Atlantic City, New Jersey).
2 Lancaster, L., Lynch, B. M., Mac Eachern, A. M., Donini, J. C., Hamza, H. , and Michaelian, K. H. *Abstract 158, 57th Colloid & Surface Science Symposium, American Chemical Society*; 1983 (Toronto, Canada).
3 Lynch, B. M., and Mac Eachern, A. M. *Proc. 1983 Conference on Coal Science*, pp.653-654.
4 Lynch, B. M., Lancaster, L., Mac Eachern, A. M., and Khan, M. A. *Paper 161, Eastern Analytical Symposium, American Chemical Society*; 1983 (New York City, U. S. A.).
5 Lynch, B. M. *Bull. Am. Phys. Soc.* 1985, **30**, 504.
6 Lynch, B. M. *Proc. Soc. Photo-Optical Instr. Engineers* 1985, **553**, 320.
7 Lynch, B. M., Lancaster, L., and Fahey, J. T. *Prepr. Div. Fuel Chem. Am. Chem.Soc.* 1986, **31**, 43.
8 Cooke, N. E., Fuller, O. M., and Gaikwad, R. P. *Fuel* 1986, **65**, 1254.
9 Rhoads, C. A., Senftle, J. T., Coleman, M. M., Davis, A., and Painter, P. C. *Fuel* 1983, **62**, 1387.
10 Stock, L. M. and Wang, S. H. *Prepr. Div. Fuel Chem. Am. Chem.Soc.* 1986, **31**, 49.
11 Fredericks, P. M., Osborn, P. R., and Swinkels, D. A. J. *Fuel* 1984, **63**, 139.
12 Larsen, J. W., and Schmidt, T. E. *Fuel* 1986, **65**, 131

Table 1

Coal Samples Subjected to High-Pressure Oxidations

Analytical and Fluidity Data on Fresh Coals

Coal Designation	Classification	C, %	H, %	O, %	Gieseler Fluidity (dd/min)
Greenhills (Western Canadian)	HV 'A'	81.56	4.75	4.79	24
Fording (Western Canadian)	HV 'A'	80.49	5.07	5.60	365
Barton (U. S. A.)	HV 'A'	81.81	5.08	4.34	20350
McClure (U. S. A.)	MV-HV 'A'	83.07	4.74	3.82	7900
Alto (Appalachian, U. S. A.)	HV 'A'	79.69	5.20	7.47	1580
Basset	L-MV	85.01	4.42	3.20	32

FIGURES

Figure 1
PAIFT Difference Spectrum
Greenhills Coal: (Oxidized 48 h) - (Fresh Coal)
Figure 2
PAIFT Difference Spectrum
Fording Coal: (Oxidized 48 h) - (Fresh Coal)
Figure 3
PAIFT Difference Spectrum
Barton Coal: (Oxidized 48 h) - (Fresh Coal)
Figure 4
PAIFT Difference Spectrum
Alto Coal: (Oxidized 48 h) - (Fresh Coal
Figure 5
PAIFT Difference Spectrum
McClure Coal: (Oxidized 48 h) - (Fresh Coal)
Figure 6
PAIFT Difference Spectrum
Basset Coal: (Oxidized 48 h) - (Fresh Coal)
Figure 7
Greenhills Coal - Carbonyl Intensity (PAIFT Spectra) vs. Oxygen %
Figure 8
Greenhills Coal - log Fluidity vs. 1690 $cm.^{-1}$ Carbonyl Intensity (PAIFT Spectra)
Figure 9
Fording Coal - log Fluidity vs. Carbonyl Intensity (PAIFT Spectra)
Figure 10
Barton Coal -log Fluidity vs. Carbonyl Intensity (PAIFT Spectra)
Figure 11
McClure Coal - log Fluidity vs. Carbonyl Intensity (PAIFT Spectra)
Figure 12
Alto Coal - log Fluidity vs. Carbonyl Intensity (PAIFT Spectra)
Figure 13
Basset Coal -log Fluidity vs. Carbonyl Intensity (PAIFT Spectra)
Figure 14
Western Canadian Bituminous Coal -
FTIR Microspectrogram of Vitrinite Component
Figure 15
Western Canadian Bituminous Coal -
FTIR Microspectrogram of Fusinite Component
Figure 16
Cape Breton Island Bituminous Coal
FTIR Microspectrogram of Vitrinite Component
Figure 17
Cape Breton Island Bituminous Coal
FTIR Microspectrogram of Kaolinite Inclusion

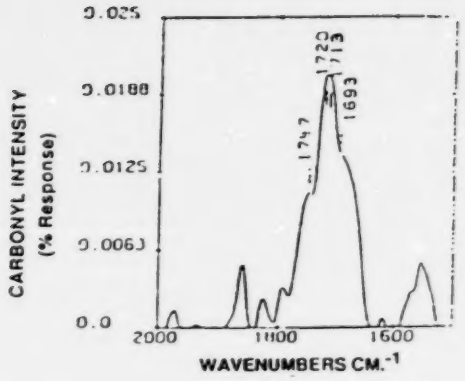


Figure 1
PAIFT Difference Spectrum
Greenhills Coal: (Oxidized 48 h) - (Fresh Coal)

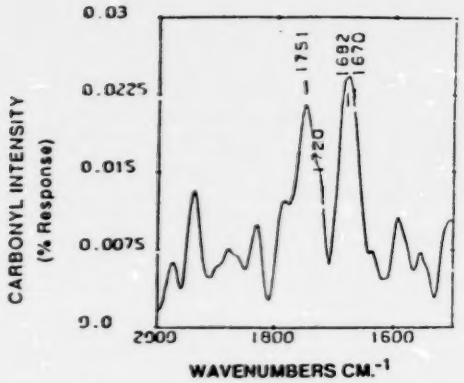


Figure 2
PAIFT Difference Spectrum
Fording Coal: (Oxidized 48 h) - (Fresh Coal)

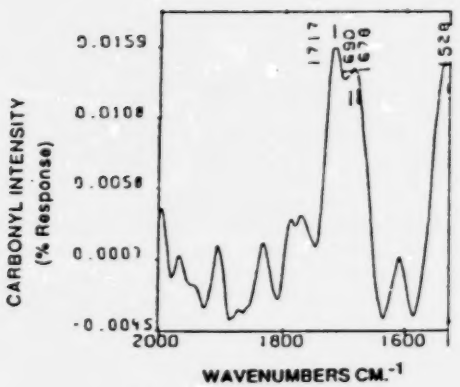


Figure 3
PAIFT Difference Spectrum
Barton Coal: (Oxidized 48 h) - (Fresh Coal)

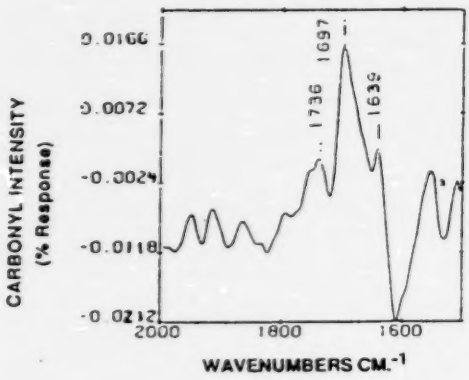


Figure 4
PAIFT Difference Spectrum
Alto Coal: (Oxidized 48 h) - (Fresh Coal)

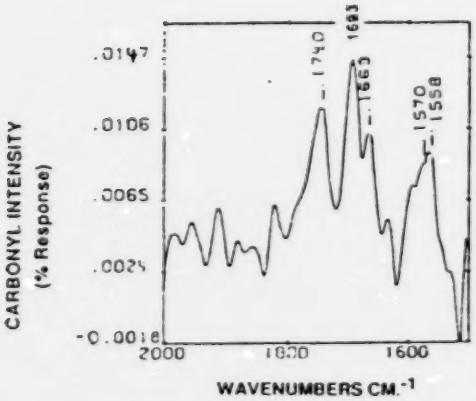


Figure 5
PAIFT Difference Spectrum
McClure Coal: (Oxidized 48 h) - (Fresh Coal)

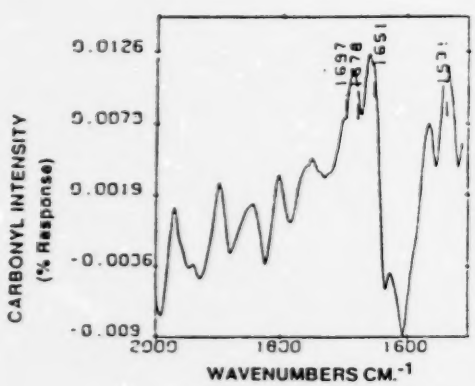


Figure 6
PAIFT Difference Spectrum
Basset Coal: (Oxidized 48 h) - (Fresh Coal)

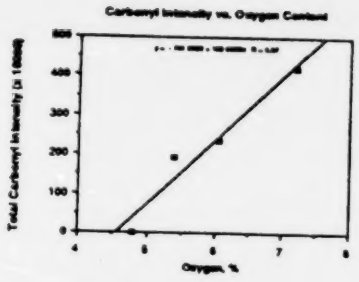


Figure 7
Greenhills Coal - Carbonyl Intensity (PAIFT Spectra) vs. Oxygen %

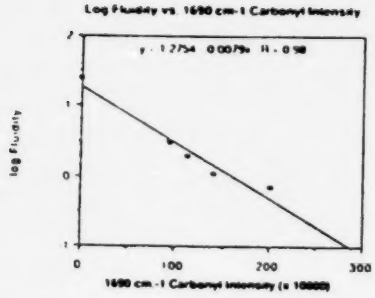


Figure 8
Greenhills Coal - log Fluidity vs. 1690 $cm.^{-1}$ Carbonyl Intensity (PAIFT Spectra)

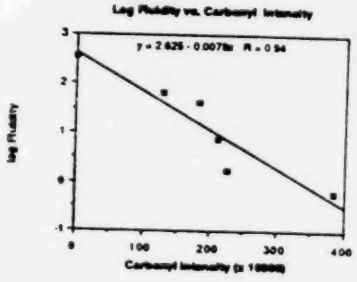


Figure 9
Fording Coal - log Fluidity vs. Carbonyl Intensity (PAIFT Spectra)

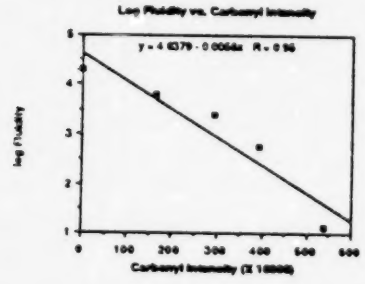


Figure 10
Baron Coal -log Fluidity vs. Carbonyl Intensity (PAIFT Spectra)

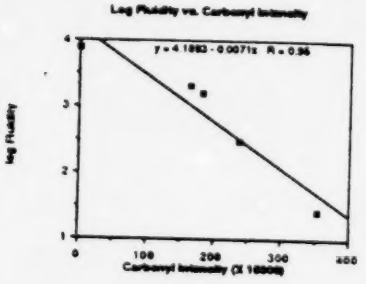


Figure 11
McClure Coal - log Fluidity vs. Carbonyl Intensity (PAIFT Spectra)

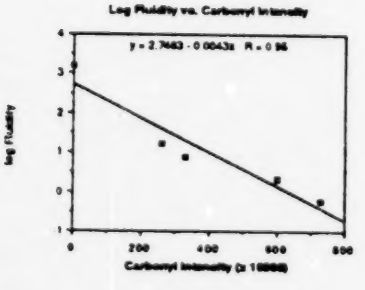


Figure 12
Alto Coal - log Fluidity vs. Carbonyl Intensity (PAIFT Spectra)

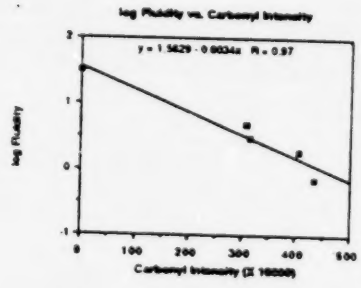


Figure 13
Basset Coal -log Fluidity vs. Carbonyl Intensity (PAIFT Spectra)

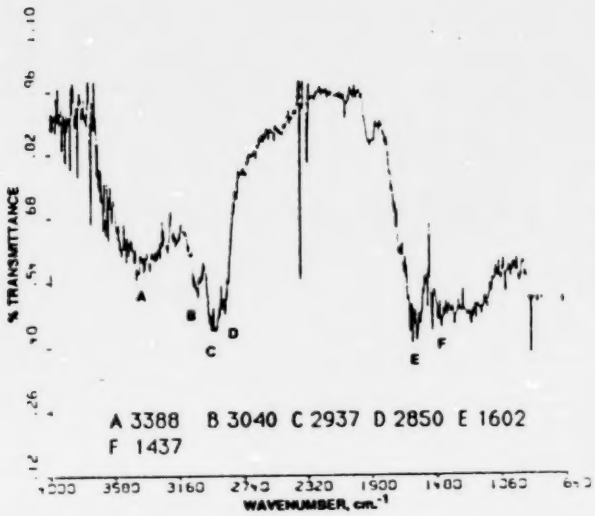


Figure 14

Western Canadian Bituminous Coal

FTIR Microspectrogram of Vitrinite Component

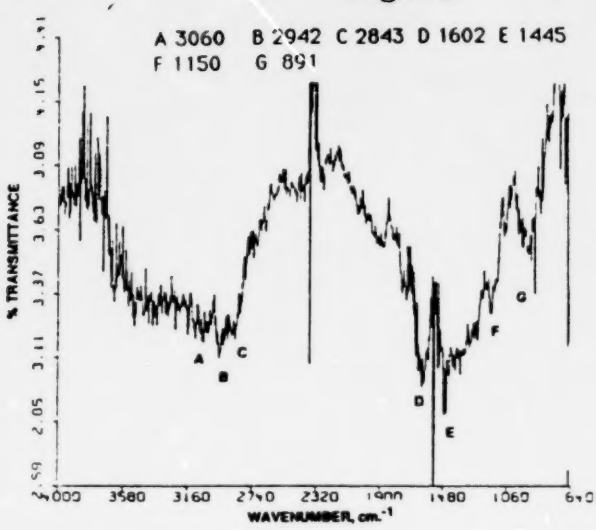


Figure 15

Western Canadian Bituminous Coal

FTIR Microspectrogram of Fusinite Component

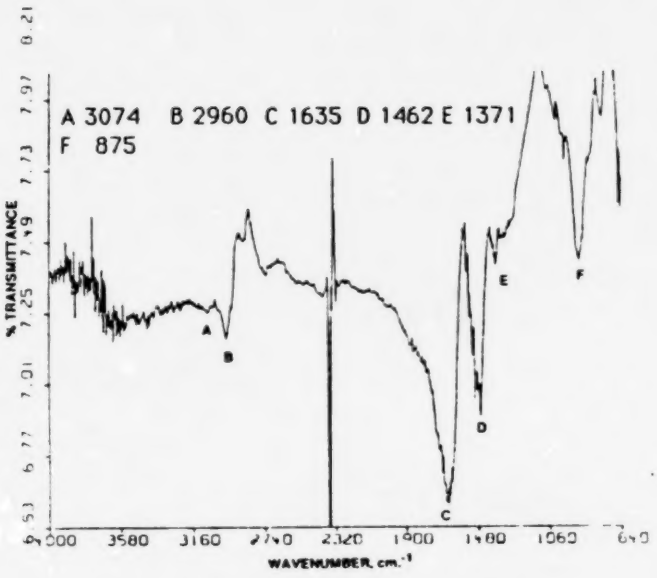


Figure 16

Cape Breton Island Bituminous Coal

FTIR Microspectrogram of Vitrinite Component

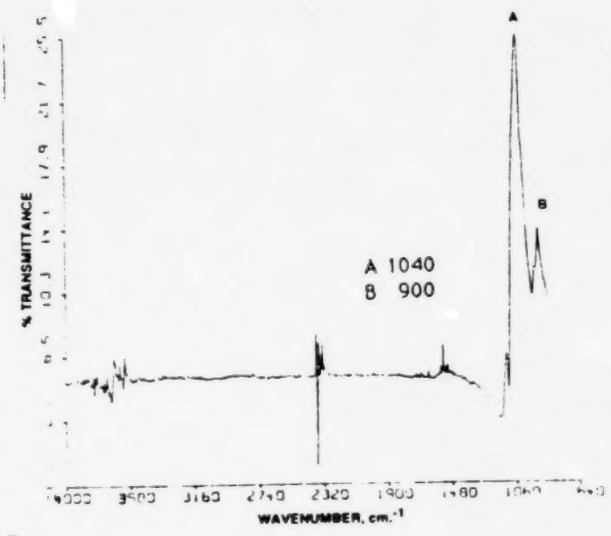


Figure 17

Cape Breton Island Bituminous Coal

FTIR Microspectrogram of Kaolinite Inclusion

4.

CHARACTERIZATION OF SURFACE FUNCTIONALITY OF COALS BY PHOTOACOUSTIC FTIR SPECTROSCOPY, REFLECTANCE INFRARED MICROSPECTROMETRY, SCANNING ELECTRON MICROSCOPY/SECONDARY ION MASS SPECTROMETRY, AND X-RAY PHOTOELECTRON SPECTROSCOPY,

BY

Brian M. Lynch, J. Anthony MacPhee, and Ronald R. Martin,

to be published in the

Proceedings of the 1987 International Conference on Coal Science,

October 1987.

PAPER ACCEPTED FOR PRESENTATION AT THE INTERNATIONAL CONFERENCE ON COAL SCIENCE, MAASTRICHT, THE NETHERLANDS, October 1987

CHARACTERIZATION OF SURFACE FUNCTIONALITY OF COALS BY PHOTOACOUSTIC FTIR SPECTROSCOPY, REFLECTANCE INFRARED MICROSPECTROMETRY, SCANNING ELECTRON MICROSCOPY/SECONDARY ION MASS SPECTROMETRY, AND X-RAY PHOTOELECTRON SPECTROSCOPY

Brian M. Lynch (1), J. Anthony MacPhee (2), and Ronald R. Martin (3)

(1) Department of Chemistry, St. Francis Xavier University, Antigonish, Nova Scotia B2G 1C0 (Canada)

(2) Energy Research Laboratories, CANMET, Energy, Mines, and Resources Canada, Ottawa, Ontario K1A 0G1 (Canada)

(3) Department of Chemistry, The University of Western Ontario, London, Ontario N6A 5B7 (Canada)

INTRODUCTION

We have applied the following recent sensitivity enhancements in spectroscopy, which promise more specific characterization of functional groups in coals and their chemical transformations, and increases in our ability to predict coal properties:

1.PhotoAcoustic Infrared Fourier Transform spectroscopy

2. Reflectance Infrared Microspectrometry

3. Scanning Electron Microscopy and Secondary Ion Mass Spectroscopy

4. X-Ray Photoelectron Spectrometry

DISCUSSION AND RESULTS

1. PhotoAcoustic Infrared Fourier Transform Spectroscopy

This technique has been developed by the group at St. Francis Xavier University over the past six years (1-5). Among the advantages it possesses for study of coals are avoidance of sample preparation, insensitivity of signal to degree of subdivision, and sensitivity to surface features generated by chemical transformations. Sloping baselines typical of pellet FTIR spectra are absent, and subtraction to yield difference spectra revealing introduced features avoids arbitrary scaling procedures. Recently, we reported (2-5) detection of carbonyl oxygen functions at the surfaces of powdered bituminous coals, derived from base-promoted or thermal decompositions of precursor peroxide species, present as ubiquitous surface entities for all except the most freshly prepared samples. The present report expands on our discovery that specific thermal decompositions accompany a standard vacuum drying procedure.

The sensitivity of conventional FTIR spectroscopy in detecting oxidative change in coals is much less than that of standard plasticity tests; thus, Painter's group (6) found less than 1 % increase in the ratioed intensity of carbonyl bands for coals oxidized at $60^{o}C$ or $140^{o}C$ for periods sufficient to decrease Gieseler fluidity by over 90 %. We have accelerated oxidative changes by subjecting six samples of representative Canadian and U. S. A. bituminous coals (see Table 1) to pressurized air at slightly elevated temperatures.

With such samples, difference spectra reveal distinct, readily resolved carbonyl peaks (around 1750, 1720, 1690, and 1650 $cm.^{-1}$) whose relative proportions are different for different coals, and we propose that the carbonyl species are generated by the standard vacuum drying procedure from specific thermal decomposition of peroxide species. Representative peak intensities in difference spectra taken for the six coals of Table 1 at the stage of 48 hours oxidation are reproduced in bar-graph form in Figure 1.

These peaks arise from different, specific decompositions of peroxides occupying different structural sites in the coals. The 1750 and 1720 $cm.^{-1}$ peaks are from decompositions of α-hydroperoxyethers yielding cyclic or open-chain esters: 1750 $cm.^{-1}$ from a cyclic ether precursor, and the 1720 $cm.^{-1}$ from an open-chain precursor, i.e.:

$$Ar.CH_2.O.R\text{-}(O_2,\ 55^oC,\ 9\ MPa)\text{->}Ar.CH(O.O.H).OR$$

$$Ar.CH(O.O.H).OR\text{-}(100^oC,vacuum)\text{-> }Ar.CO.O.R$$

and the 1690 and 1650 $cm.^{-1}$ peaks from decompositions of α-hydroperoxy-aralkanes or -diarylalkanes, i.e.:

$$Ar.CH_2.R\text{-}(O_2,\ 55^oC,\ 9\ MPa)\text{-> }Ar.CH(O.OH)R$$

$$Ar.CH(O.OH)R\text{ -}(100^oC,\ vacuum)\text{-> }Ar.CO.R$$

$$Ar.CH_2.Ar\text{ -}(O_2,\ 55^oC,\ 9\ MPa)\text{-> }Ar.CH(O.OH)Ar$$

$$Ar.CH(O.OH)Ar\text{ -}(100^oC,\ vacuum)\text{-> }Ar.CO.Ar$$

The relative proportions of the four carbonyl absorptions for the six coals examined are dependent in a complex manner upon oxygen content, carbon/hydrogen ratio, and the progress of oxidation, but there are quantitative associations of increasing carbonyl intensities with many characteristics of the sequences of oxidized samples for a given coal.

As examples, linear relationships link total thermally generated carbonyl intensity and (directly determined) oxygen content, illustrated for the bituminous high-volatile 'A' coal A-1 (Appalachian) in Figure 2, and linear relationships link the thermally developed carbonyl intensities to the logarithms of the Gieseler fluidities for all six coals (Table 2). There is also a positive, quantitative, correlation between the initial oxygen content of the coal samples and the "snapshot" of developed carbonyl intensity after 48 h oxidation (Figure 3). The rates of appearance of the various types of carbonyl species for a given coal are, in general, linearly related to one another (Figure 4).

However, the coals behave in sufficiently different fashions (both in quantitative distribution of the various introduced carbonyl species, in qualitative rates of generation, and in the nature of the influence of changed functionality on the technical properties) that generalized treatment as a single data set would obscure the individual correlations.

We suggest that caution is appropriate in applying (to North American coals) the approaches adopted by Fredericks and co-workers (7) where generalized predictions of technological properties are made using principal factor analyses of FTIR spectra of a wide range of coals.

2. Reflection FTIR Microspectrometry

We have conducted preliminary examinations of sectioned, polished surfaces of samples of Canadian bituminous coals using the IR-PLAN accessory in the reflectance mode. Representative spectra will be illustrated. Differences among the microscopically distinguishable components, and the ease of detection and identification of mineral inclusions, suggest that direct examinations of coals undergoing chemical transformations (such as discussed in this paper and our earlier work) could be examined profitably using this accessory FTIR device.

3. Scanning Electron Microscopy/Secondary Ionization Mass Spectrometry

This work was carried out at the University of Western Ontario (for leading references, see 8, 9). Coupling of these two techniques allows visualization of specific regions of the coal surfaces, and identification of the spatially distributed images of various polyatomic species associated with oxidative and thermal changes will be illustrated. Distributions of acidic and peroxidic oxygen functions have been mapped by surface reactions with barium hydroxide and/or diamminesilver ion.

4. X-Ray Photoelectron Spectrometry: Trifluoroacetylation as a Derivatization Technique

Infrared analysis of hydroxyl content of coals through acetylation via acetic anhydride/pyridine is a common method, but its quantitative nature and selectivity are doubtful. Since difficulties arise in part from peak overlap of acetate carbonyl with the 1600 cm.-1 absorption of coals, we explored trifluoroacetylation (the carbonyl absorbs around 1800 cm.$^{-1}$) as an alternate technique.

The trifluoroacetate ion may be analyzed readily by anion chromatography after hydrolysis, and quantitation of the trifluoroacetyl group should be possible by calibration against the intensity of the fluorine and trifluoromethyl-carbon signals in the X-ray photoelectron spectra of such samples. However, our preliminary work(to be illustrated) shows that side reactions involving insertion of -CF2- moieties into the coal accompany thermal O-trifluoroacetylation reactions.

EXPERIMENTAL METHODS

PhotoAcoustic Infrared Fourier Transform Spectra

Spectra were obtained using a Bruker IFS110 purge-type Infrared Fourier System. Full experimental details are given in references 2-5. Coal samples were ground to the range 50-60 mesh under nitrogen, subjected to oxidation by air at 55C and 9 MPa for periods ranging from 3 to 196 h, and dried at 100^{o}C under vacuum for 6 h before transfer to the sample cup of the photoacoustic accessory. Analytical and fluidity data on the as-received coal samples are presented in Table 1.

Reflectance FTIR Microspectrometry

Spectra were acquired (250-500 scans) using an IR-PLAN accessory and a Nicolet 20SX spectrometer, at a resolution of 4 cm.$^{-1}$; spectra are referenced against an equivalent area of a gold-surfaced mirror. We thank Cindy Friedman of Spectra-Tech, Inc., for these measurements.

X-Ray Photoelectron Spectrometry

Measurements were made through the courtesy of Dr. J. R. Brown, Energy Research Laboratories, CANMET.

Scanning Electron Microscopy/Secondary Ionization Mass Spectrometry

Measurements were made at Surface Science Western, University of Western Ontario.

CONCLUSIONS

We have indicated the potential for surface characterization of several techniques under study in our laboratories. We suggest that the evidence for previously unquantified and undetected peroxide species on coal surfaces presented above and earlier (2-5) requires reconsideration of the influence of the proportion of surface peroxides upon the course(s) of coal pyrolyses, and provides strong support for the procedures being adopted for the U. S. Department of Energy's Premium Coal Bank.

ACKNOWLEDGEMENTS

The work upon which this paper is based was supported by Energy, Mines, and Resources Canada through Research Contracts to St. Francis Xavier University and the University of Western Ontario.

REFERENCES

1 B. M. Lynch and A. M. Mac Eachern, Proc. 1983 Conf. Coal Sci., 653.

2 B. M. Lynch, L. Lancaster, and J. T.Fahey, Prepr. Div. Fuel Chem. Am. Chem.Soc. 31 (1986) 43.

3 B. M. Lynch, L. Lancaster, and J. A. MacPhee, Fuel 66 (1987) in press.

4 B. M. Lynch, L. Lancaster, and J. A. MacPhee, Prepr. Div. Fuel Chem. Am. Chem.Soc. 32 (1987) 138.

5 B. M. Lynch and J. A. MacPhee, Chapter 4: Photoacoustic FTIR Spectroscopy in Detection of Coal Oxidation, in: C. R. Nelson, Ed., Chemistry of Coal Weathering, Elsevier, Amsterdam, 1987.

6 C. A. Rhoads,, J. T. Senftle, M. M. Coleman, A.Davis, and P. C. Painter, Fuel 62 (1983) 1387.

7 P. M. Fredericks, P. R. Osborn, and D. A. J. Swinkels, Fuel 63 (1984) 139.

8 R. R. Martin, B. Wiens, N. S. McIntyre, B. Kronberg, and J. A. MacPhee, Fuel 65 (1986) 1024.

9 N. S. McIntyre, R. R. Martin, W. J. Chauvin, C. G. Winder, J. R. Brown, and J. A. MacPhee, Fuel 64 (1985) 1705.

Table 1

Coal Samples Subjected to High-Pressure Oxidations

Analytical and Fluidity Data on Fresh Coals

Coal	Classification	C, %	H, %	O, %	GieselerFluidity*
C-1(Western Canadian)	HV 'A'	80.49	5.07	5.60	365
C-2(Western Canadian)	HV 'A'	81.56	4.75	4.79	24
A-1 (U. S. A.)	HV 'A'	79.69	5.20	7.47	1580
A-2 (U. S. A.)	HV 'A'	81.81	5.08	4.34	20350
A-3 (U. S. A.)	MV-HV 'A'	83.07	4.74	3.82	7900
A-4 (U. S. A.)	L-MV	85.01	4.42	3.20	32

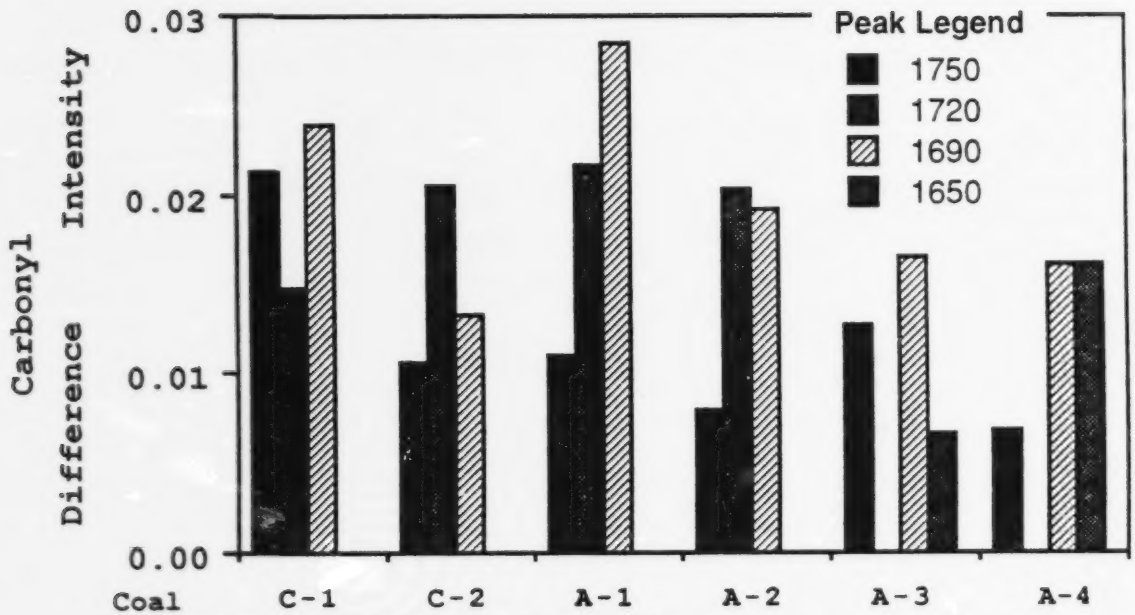
*dial divisions/minute @ 400^{o}C.

Table 2

Relationships between Gieseler Fluidity and Thermally Generated Carbonyl Intensities for the Coals of Table 1

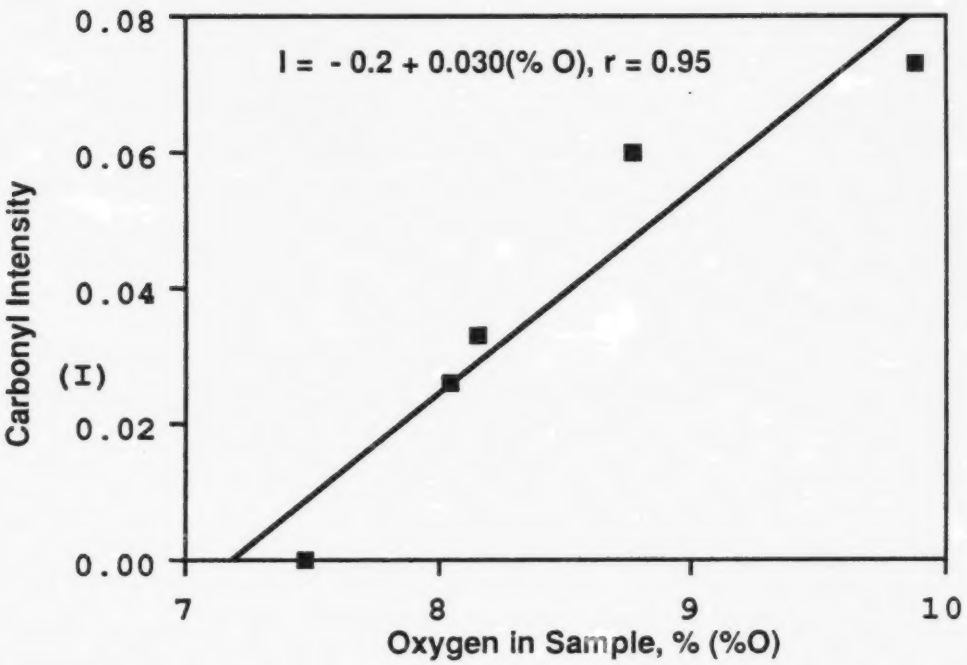
Coal	log Fo (obs)	log Fo(calc)	slope*	n	Correlation coefficient, r
C-1	2.56	2.64	79.1	6	0.94
C-2	1.38	1.27	79.5	5	0.98
A-1	3.20	2.74	43	5	0.95
A-2	4.31	4.63	56	5	0.95
A-3	3.90	4.06	116	5	0.98
A-4	1.51	1.56	34	5	0.97

*log F = log Fo + slope (Carbonyl intensity)



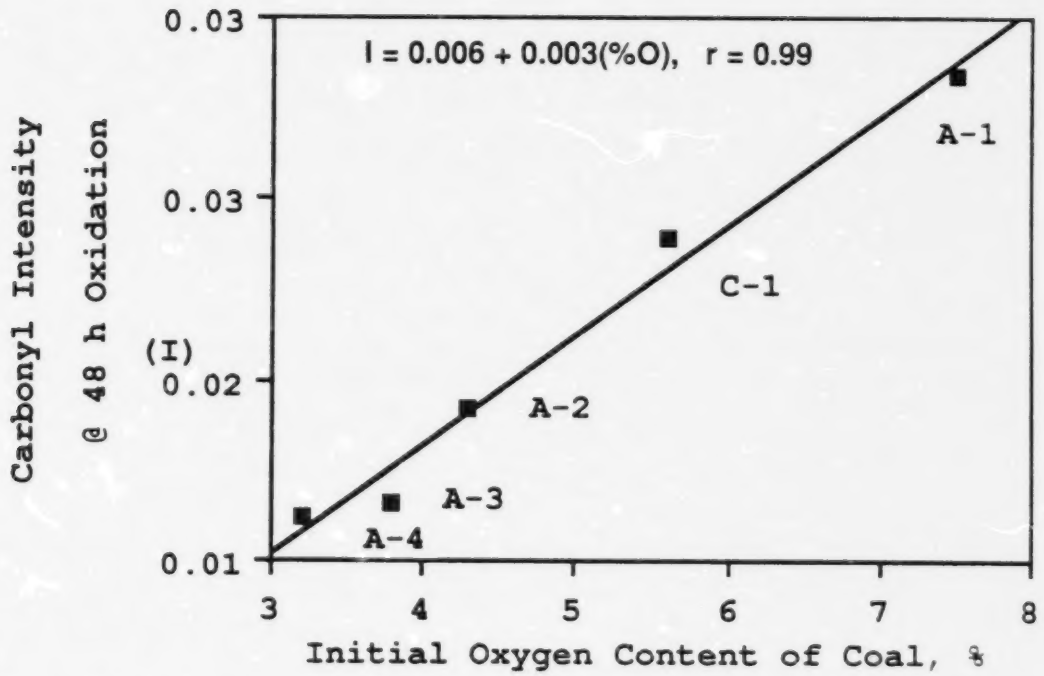
Distribution of C:O Peak Intensities, 6 coals oxidized for 48 h

Figure 1

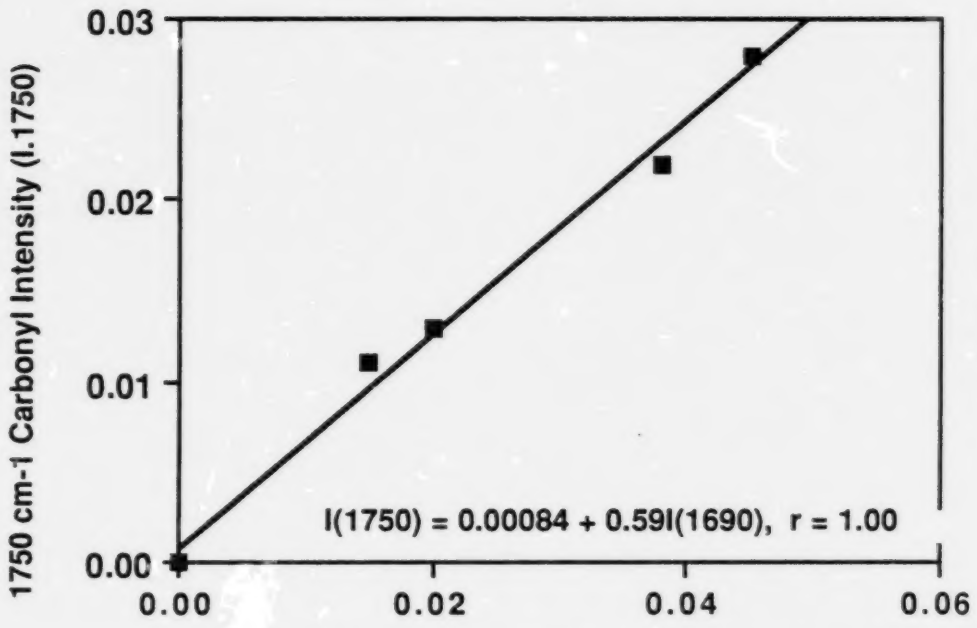


Coal A-1, Carbonyl Intensity vs. % Oxygen

Figure 2



Carbonyl Intensity/Oxygen Correlation, Five Coals
Figure 3



Coal A-1, Relationship b/w Carbonyl Intensities

Figure 4